

The Ageing of PA-11 in Flexible Pipes

API TECHNICAL REPORT 17TR2
FIRST EDITION, JUNE 2003



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Upstream Segment

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The Ageing of PA-11 in Flexible Pipes

1 Introduction

In the construction of a flexible pipe, an inner polymeric pressure sheath is the only layer which seals the conveyed fluid within the pipe structure. Therefore, its integrity is crucial to safe and reliable operation. Polyamide 11 (PA-11) is the most commonly used pressure sheath material⁽¹⁾, other options being polyvinylidene fluoride and polyethylene.

This document provides comprehensive guidance on materials and pipe issues regarding the use and operation of PA-11 in flexible pipe applications, typically in production and gas handling applications up to 100°C.

The document concentrates on the use of PA-11 in the internal sheath of flexible pipes, although similar considerations may also apply to other uses of PA-11 within flexibles, e.g., anti-wear layers, intermediate sheathes and outer sheathes.

The collective goal of this document is to prevent failure of the internal pressure sheath, as a result of ageing and associated loss of mechanical properties, by determining and disseminating the necessary scientific and practical information. API Specification 17J and Recommended Practice 17B^(2,3) contain only limited information with respect to these phenomena, and this report supplements and updates the data in the Third Edition of API RP 17B⁽³⁾.

PA-11 is also used in umbilicals. However, the exposure temperatures are frequently lower than production temperatures. In cases of higher temperature exposure, the information contained in this document applies.

2 The Ageing of PA-11

2.1 BACKGROUND

The main ageing concern regarding PA-11 in flexible pipe applications, in the absence of oxygen in the bore fluids, is the effect of water at elevated temperature. The hydrolysis reaction breaks the polyamide links within the polymer, and leads to embrittlement of the material. There is a long history of detailed study of this process, and key references are listed in Appendix A.

Pipe manufacturers all use slightly different grades of RilsanTM PA-11. These differences mainly concern the product specifications and processing parameters defined by each manufacturer. It should be noted, however, that two antioxidant packages have been used within RilsanTM PA-11 over the years, both having been fully qualified according to API Specification 17J requirements. All data included in this document is based on experience with PA-11 with the old antioxidant package. The industry expects that the working life of the PA-11 with the new antioxidant package is expected to be at least comparable to that with the old package, as the basic polymer remains unchanged. The ageing and definition of

appropriate acceptance criteria for the PA-11 with the new antioxidant are currently subject to further investigation and quantification to assure at least equivalent ageing performance. Therefore it is assumed that the same service life prediction method can be used for all PA-11 pipe.

The rate of the PA-11 ageing reaction is highly dependent on a number of operational factors including the water content of the fluid, temperature, acidity (due to carbon dioxide, hydrogen sulphide, organic acids, inorganic acids), oil composition, and presence of oilfield treatment chemicals, such as methanol. Considerations regarding the chemical ageing of PA-11 are detailed in Appendix A, and summarised in the sections which follow. Outline guidelines for conducting laboratory ageing experiments are given in Appendix B.

It should be noted that other aspects of performance, unrelated to chemical ageing, may influence the use of any polymeric material in a flexible pipe, e.g., mechanical properties, fracture toughness, creep, blistering performance, coefficient of friction, thermal expansion, dynamic properties, etc. These other aspects of performance are outside the scope of this document.

2.2 THE EFFECT OF WATER IN SATURATED & UNSATURATED CONDITIONS

Experimental results derived through JIP projects and in-house research along with fundamental chemistry considerations confirm that the process affecting the ageing of PA-11 in a water environment is reduction in the molecular weight due to hydrolysis. This process is independent of the sheath thickness in typical pipe designs. There is now good agreement on this aspect of ageing from different sources. The chemical mechanisms are discussed in Appendix A.

If there is free water in a production stream, the PA-11 will age as if immersed in 100% water. It has also been found that a free water phase is not necessary for such ageing to occur. Conditions should be regarded as “wet” for the consideration of PA-11 ageing if water levels are > 80% of saturation in any given liquid or gas environment flowing within the pipe⁽³⁾.

2.3 THE EFFECT OF THE pH OF WATER

The ageing of PA-11 is accelerated in the presence of acid, under typical field operating conditions. Again, the chemical mechanisms are discussed in detail in Appendix A.

The effect of carbon dioxide is to lower the pH of produced water, and so this must be taken into account in PA-11 ageing. The effect of H₂S on pH can be similarly accounted for. pH can be both calculated and measured. There are several reliable industry and proprietary programs for calculation of pH, based on partial pressures (fugacity), temperature and water chemistry. Direct pH measurement can be very complicated. To

reflect in-situ operating conditions it must be carried out under pressure in order to account for the effect of the acid gases.

Consideration of using either the partial pressure (and/or fugacity) of acid gases or pH of the water phase in determining the effect of acid gases on PA-11 ageing is currently under further investigation. Within this document, pH calculated using full water analysis is employed.

There may also be a contribution to the pH of the water phase from acids in the oil phase, although there may also be other effects of such acids, as described in the following section.

2.4 THE EFFECT OF DIFFERENT CRUDES

Different crude compositions may affect PA-11 differently. The most important ageing effect is derived from the so-called TAN (Total Acid Number) of the crude, rather than pH, which applies only to the water phase. TAN is a gross measure of the amount of organic acids, typically naphthenic carboxylic acids, within the crude⁽⁴⁾.

The effects of TAN are generally secondary relative to the effects of water and pH. The principal effect of these high molecular weight acids, which are not soluble in water, is to give an extra "skin" effect, effectively a highly aged surface layer, on top of the pH effect. Specific ageing testing may be required for very highly acidic crudes (TAN > 3.5).

In order to quantify the effect of a specific crude on PA-11 it may be necessary to gain a more detailed knowledge of the acid species. Different ageing effects have been observed at similar TAN numbers.

2.5 THE EFFECT OF HYDRATE TREATMENT CHEMICALS

Hydrate treatment chemicals may affect the ageing of PA-11.

Pure, liquid methanol diffuses easily and quickly through PA-11 and very effectively extracts plasticiser and swells the material.

As a hydrate prevention and remediation measure, methanol is typically introduced either by continuous injection or in batch treatments. In continuous injection, the temperature is typically high, e.g., the production temperature if injected at a production wellhead, but the concentration is low. In batch treatments, the average exposure temperature may be lower than the production temperature, but the methanol is in high concentration. It should be noted that methanol used in the field varies in its water content, and is typically only specified to be > 95% methanol. The contribution of methanol to the ageing of a PA-11 internal pressure sheath must take account of all these factors.

For continuous injection, at low concentrations, typically 10 to 200 ppm, field experience suggests that methanol is not a problem. For PA-11 pressure sheath service life prediction under these conditions the effect of methanol can be neglected.

For batch treatment, an estimation of cumulative exposure time and temperature must be made. Until other data

becomes available, extrapolation of high temperature test data to lower operating temperature can then be used to give a conservative indication of the effect of the batched methanol on a PA-11 pressure sheath.

The detailed effects of methanol are subject to further investigation.

Glycols are also widely used offshore, e.g., MEG for hydrate inhibition and TEG for gas drying. Glycols do not diffuse into PA-11 as quickly as methanol, and do not cause major swelling. Conservatively, the ageing effect is comparable to water at pH = 7. Operators should be aware of the potential effects of acids created during glycol regeneration.

2.6 THE EFFECT OF TREATMENT CHEMICALS

Many different types of production chemical can be deployed in the oilfield, some of which can have an effect on PA-11. The method of deployment is important. Table 1 has been prepared by considering data derived mainly from testing of umbilicals. It should be taken as giving preliminary guidance only. If there is any doubt about compatibility with production chemicals, then specific evaluation should be carried out.

2.7 OTHER EFFECTS ON CHEMICAL AGEING

2.7.1 Wax and Scale

The effect of wax and scale is as yet undefined, although there is some evidence to suggest that they may increase pressure sheath life, e.g., as thermal barrier. This is, however, difficult to consider in either initial pipe design or operation.

2.7.2 The Effect of Treatment Fluids Trapped Behind the Carcass

It has been shown that in some circumstances, fluids can be trapped behind the internal steel carcass giving a localised environment. While this is not thought to be a problem in liquid service, gas pipes may need to take account of this. For example, in a gas pipe batch treated with methanol, the ageing effect of the methanol must take account of the time needed to evaporate methanol trapped behind the carcass. Heavier alcohols such as MEG may never evaporate from behind the carcass once there.

2.7.3 Effect of Fluids Absorbed During Storage and Hydrotest

The ageing effect of water absorbed during storage and hydrotest will be minimal, as PA-11 naturally saturates under ambient conditions, natural absorption being 1 to 2 %, dependent on temperature. The potential effects of any chemical package, e.g., corrosion inhibitors, biocides, glycols, added to the water should be considered.

Table 1

Production Chemical	Chemical Nature	Continuous Injection	Effect of Neat Chemical
Scale inhibitor	Acrylate polymers or phosphates/phosphonates in aqueous solution, with ether and alcohol additions. Generally acidic.	No effect	PA-11 pressure sheath not normally in contact with neat chemical, but phosphonates can be aggressive.
Pour point depressants/wax inhibitors	Ethylene Vinyl Acetate copolymers in solvents	No effect	No effect. PA-11 pressure sheath not normally in contact with neat chemical.
Demulsifier	Alkoxylated phenol formaldehyde, in solvents	No effect	PA-11 pressure sheath not normally in contact with neat chemical.
Aromatic solvents	Benzene, toluene, xylene	No effect	Swelling above 40°C. Minimise exposure.
Drag reducing agents	Very high molecular weight polyalphaolefins and polyacrylamides.	No effect	No effect. PA-11 pressure sheath not normally in contact with neat chemical.
Ca carbonate scale dissolver	Strong inorganic acids, Na EDTA and alternatives	Not used in dilute form	Strong inorganic acids should not be used in PA-11 pipe.
Ba sulphate scale dissolver	Strong alkalis	Not used in dilute form	Strong alkalis above pH = 10 should not be used in PA-11 pipe.
Wax & asphaltene dissolvers	Aromatic solvents, e.g., xylene, or terpene based solvents, e.g., based on leminene	No effect	Aromatic solvents can cause swelling above 40°C. Minimise exposure.
Hydrate inhibitor	Neat alcohol, normally methanol or glycol, but may be ethanol	See section 2.5	See section 2.5.
NaOH	Hydrate inhibition	Not used in dilute form	Strong alkalis above pH = 10 should not be used in PA-11 pipe.
Corrosion inhibitor	Ethoxylated and quaternary amines in aqueous glycols or alcohols. pH in range 4 – 8	No effect	PA-11 pressure sheath not normally in contact with neat chemical, but will be aggressive and should be avoided.

Note: Storage of umbilicals containing glycol or methanol at high ambient temperature has resulted in plasticiser extraction, which was later observed in the fluid⁽⁵⁾.

2.7.4 The Consequences of Outer Sheath Damage

Mechanical damage of the outer sheath may expose the internal or intermediate pressure sheath to seawater, and any fluids used to treat the flooded annulus for anti-corrosion purposes. Where outer sheath damage occurs, there is therefore a need to evaluate the effect of seawater and any other chemicals in the pipe annulus.

Typically, where a pipe is being used to handle wet fluids, seawater will not affect the ageing process on the internal surface of the pressure sheath, but may effect the ageing profile across the sheath. Where a pipe is being used to handle dry fluids, an ageing profile will be created across the sheath,

with the most highly aged material within the pressure sheath thickness rather than on the internal surface.

2.8 DETERMINATION OF AGEING

The chemical ageing of PA-11 can be followed in a number of ways. In common with other semi-crystalline polymers, for PA-11 grades employed in flexible pipes, there is a critical average molecular weight (MW) range over which there is a transition in mechanical properties. Above this molecular weight range, the material behaves in a highly ductile fashion. Below it, it is much more brittle. As a result, chemical ageing of PA-11 can be followed by tracking molecular weight^(6–9).

Mechanical properties, such as elongation at break, have been used to follow the ageing of PA-11, and indeed API RP 17B suggests a minimum acceptable elongation to break of 50%. However, measurement of elongation at break in this material is subject to a number of difficulties, including the

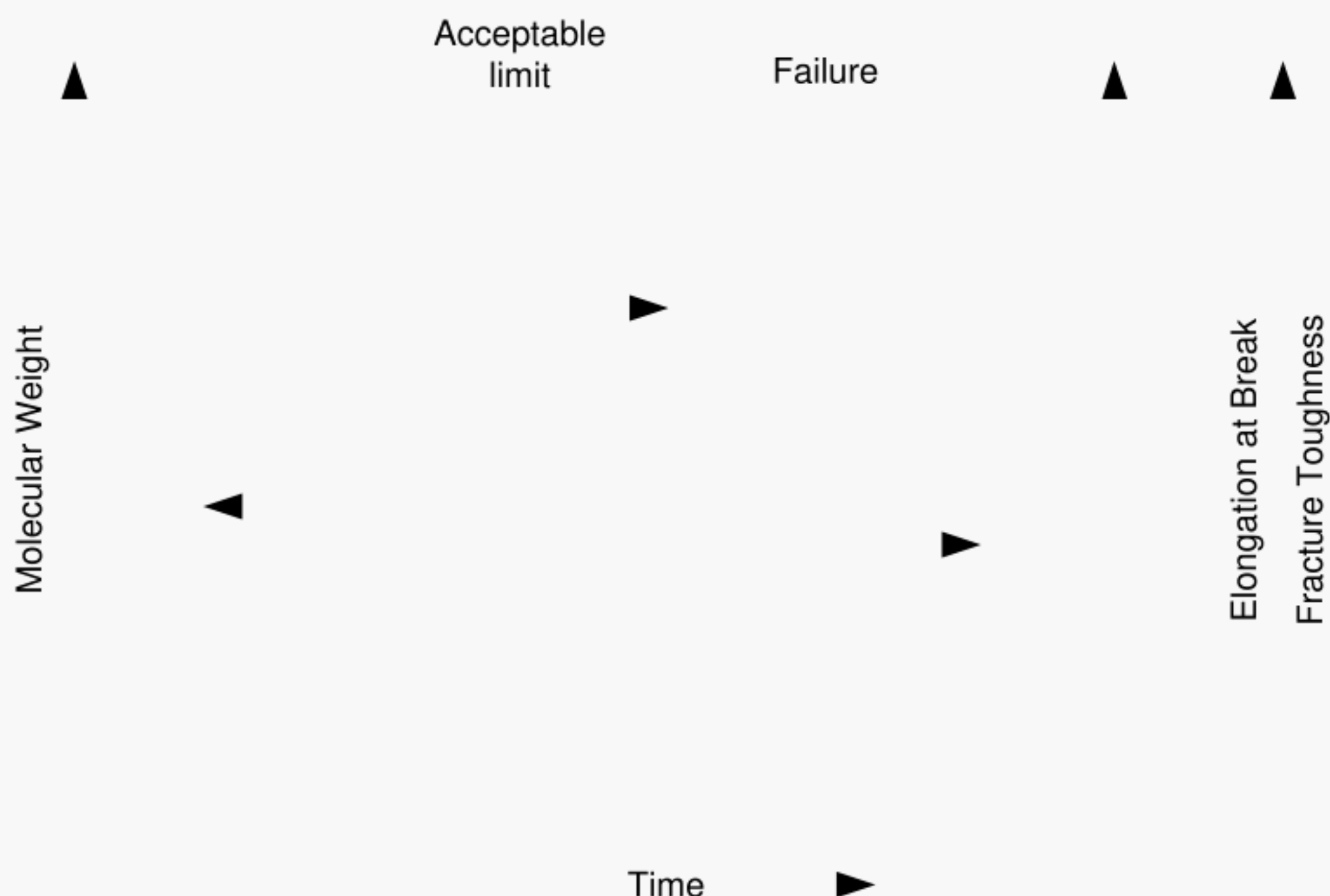


Figure 1—Illustration of the Transition in Mechanical Properties and MW with Time

need to use numerous, large samples, the fact that the tests are destructive, and the fact that test samples are very susceptible to mechanical damage during machining. However, the biggest problem with this method is that it does not detect the extent of ageing until the material has entered the stage where it begins to experience the sharp change in properties at the ductile-brittle transition. Other mechanical property measurements, such as fracture toughness, have been much less studied in flexible pipe applications, but may offer advantage over elongation at break.

In contrast, molecular weight, and its associated experimentally measured properties, are able to detect changes throughout the ageing period from new material up to and through the ductile-brittle transition. This is illustrated in Figure 1.

Therefore, the current state-of-the-art is such that molecular weight has been adopted for service life assessment. A number of MW characterisation techniques exist, such as viscosity, size exclusion chromatography, light scattering, osmotic pressure or with instruments which use multiple methods and detectors. A comparison of methods for determining molecular weight can be found in Appendix C.

Inherent viscosity represents a simple, readily standardised measurement method. A test protocol for MW determination by measurement of Inherent Viscosity is to be found in Appendix D. This method was subject to a “Round-Robin” evaluation, the results of which are described in Appendix E.

3 Service Life Prediction Models

3.1 GENERAL

The service life prediction models consist of tools for predicting the ageing of PA-11 with time over field exposure, and initial acceptance criteria, based on corrected inherent viscosity, as described in 2.8.

Service life prediction tools can be used to predict changes in molecular weight and correlated properties over field life.

Typically at the preliminary design stage, where relevant operational parameters are not completely defined, as a first approach, a Miner’s type rule is assumed for accumulated operational history, such as changes in temperature, water production, methanol injection etc. In this instance, the appropriate ageing curves from 3.4 can be employed.

Much more comprehensive models exist for use during detailed design and operation, which predict PA-11 pressure sheath life, based on detailed planned or actual operational exposure. These models are based on the rigorous chemical and physical considerations outlined in Appendix A.

3.2 INPUT PARAMETERS

In order to utilise the models, both material and operational data are needed.

For design of new pipes, a corrected inherent viscosity of 1.8 dl/g should be used as the initial value. An end user may accept the use of a higher initial value for design after

detailed review of the manufacturing history of a specific flexible pipe supplier.

For evaluation of manufactured or aged pipes, the initial molecular weight or inherent viscosity should be that measured on the manufacturing run of the actual pipe in question, according to procedures in Appendix D.

Operational data must be provided, in as much detail as possible. For example, at the design stage, a typical data set might include: temperature; water cut with time; CO₂ levels; pressure; predicted downtime; crude acidity; hot oil regime; etc. It is also necessary to include estimated cumulative exposure to production chemicals, e.g., methanol, acid etc. Temperature gradients across the pressure sheath thickness should not be considered.

Given the sensitivity of the service life models to temperature, inclusion of the temperature profile of the development over field life in any analysis can improve the reliability and accuracy of the predictions derived.

As a project moves into the operational phase, the extent and accuracy of this data should increase and PA-11 service life verification can form part of the overall flexible pipe integrity assurance process.

3.3 INITIAL ACCEPTANCE CRITERIA

The initial acceptance criterion for PA-11 pressure sheathes is based on the corrected inherent viscosity of the most highly degraded material on the inside bore of the sheath reaching a certain defined level.

It is acknowledged that in practise there may be a gradient of corrected inherent viscosity across the wall thickness of the pressure sheath. Therefore, depending upon the failure mode, consideration of only the most highly degraded material is a conservative approach.

Once the initial acceptance criterion is reached, the pressure sheath has aged significantly, as illustrated in Figure 1. In order to continue using the pipe, an analysis of potential failure modes should be performed. This will aim to evaluate the margin of safety and address risk and criticality, in a remnant life assessment, considering recovery and re-use if applicable.

The initial acceptance criteria is based on a failure criterion derived and validated from both the examination of pipe retrieved from service, detailed in Appendix F, and from laboratory mechanical property, fatigue and crack growth testing, detailed in Appendix G.

The failure criterion for a PA-11 pressure sheath is a corrected inherent viscosity of 1.05 dl/g. Therefore, the initial acceptance criterion is set at a corrected inherent viscosity of

1.2 dl/g. This initial acceptance criterion typically includes a time based safety factor of 1.6 or more over failure, e.g., 1.64 at pH = 4, 1.75 at pH = 5, and 2 at pH = 6.

It is recognised that this initial acceptance criterion is not based on a large statistical base. However, from the field failure results indicate it is conservative, and it is consistent with laboratory experience.

It should be noted that there is potentially a good case for reducing the initial acceptance criterion to 1.1 dl/g in case of static applications. There are several reasons for this:

- a. *Stress levels*—In static applications, a pressure sheath is typically only subjected to thermal stresses which are lower than 3 MPa, e.g., in the case of cool down from 75°C to 20°C. In a dynamic application, stresses as a result of vessel motion, typically range from 6 to 26 MPa, ignoring thermal stresses.
- b. *Number of cycles*—A static pipe is typically subjected to 1000 to 5000 temperature and pressure cycles over its lifetime, whereas a dynamic pipe will see a much larger number of stress cycles, typically 10⁸.
- c. *Low strain rate*—In static applications, strains rates are typically very low. There is a growing body of evidence to suggest that under such circumstances the ductile / brittle transition occurs at temperatures below those encountered in typical field conditions.
- d. *Field experience*—As shown in Appendix F, all the failures of static lines have involved PA-11 material with corrected inherent viscosity lower than 0.95 dl/g.

This case for setting a reduced initial acceptance criterion for static pipe is currently undergoing further refinement.

3.4 AGEING CURVES

The prediction curves in Figure 2 are derived from the initial acceptance criterion of CIV = 1.2 dl/g.

The mathematical relations for these curves are tabulated in Table 2.

The API RP 17B relations have been taken from close examination of Figure 21 in the Third Edition⁽³⁾. The “unsaturated” RP 17B curve is still to be employed in dry service, as defined in 2.2.

The “Batched methanol treatment” relation can be used to give a conservative indication of the effect of the batched methanol on a PA-11 pressure sheath, by considering cumulative exposure time and temperature for methanol batch treatments.

A worked example of service life prediction using these curves is included as Appendix H.

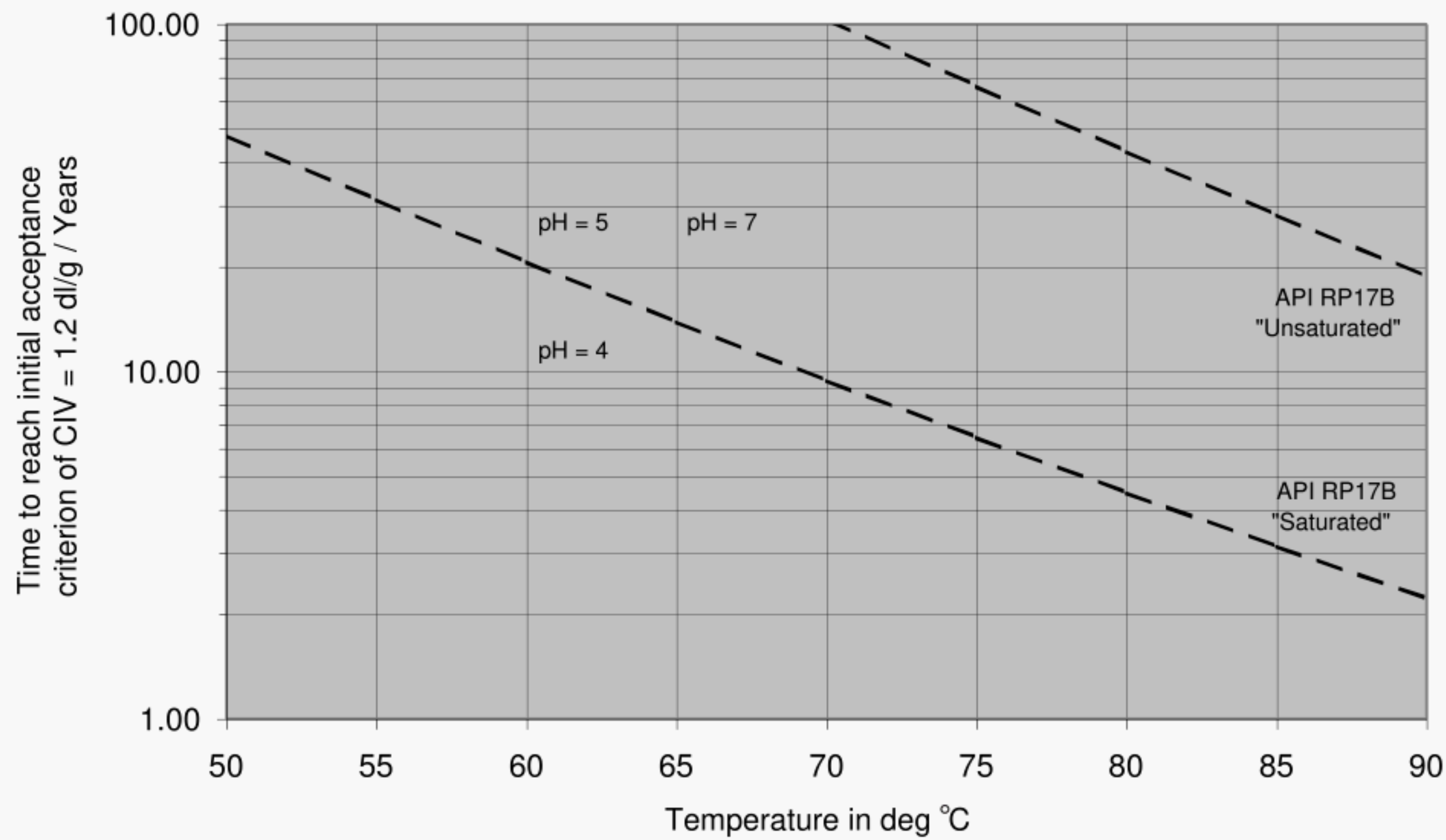


Figure 2—Time to Reach the Initial Acceptance Criterion of 1.2 dl/g

Table 2

Service condition	Mathematical relation for time to reach initial acceptance criterion of 1.2 dl/g
pH 7:	$\ln(\text{Time in years}) = 14033/T(K) - 38.383$
pH 5:	$\ln(\text{Time in years}) = 14033/T(K) - 38.974$
pH 4:	$\ln(\text{Time in years}) = 14033/T(K) - 39.259$
API RP 17B "Saturated"	$\ln(\text{Time in years}) = 8991/T(K) - 23.968$
API RP 17B "Unsaturated"	$\ln(\text{Time in years}) = 10612/T(K) - 26.300$
Batched methanol treatment	$\ln(\text{Time in years}) = 11147/T(K) - 33.032$

4 Field Monitoring of PA-11

Section 13.2.1 of API RP 17B⁽³⁾, and other international guidelines⁽⁹⁾, call for the implementation of a risk based inspection & monitoring strategy for all flexible pipes. Some outline guidance specific to polymers is currently given in 13.4.3 and 13.4.4, and this is expanded in the sections which follow here.

4.1 METHODS OF FIELD MONITORING

For PA-11 pressure sheaths, monitoring options are either “passive,” i.e., coupons of PA-11 immersed in flowing stream for removal at regular intervals (API RP 17B section 13.4.3), or “active,” i.e., dielectric sensing (API RP 17B section 13.4.4).

Under the passive options, it is possible to construct flanged spools to accommodate a number of samples held flush with the pipe ID. This has the advantage of single sided exposure of the material, but access is difficult. The alternative option is to employ a standard access fitting, with either flush coupons or a ladder rack type coupon holder. This has the advantage of simpler access using standard equipment, commonly accommodating six to ten samples on a single probe, all exposed from all sides. A flush coupon exposes a very limited amount of material, but has the advantage of single sided exposure of a thickness equivalent to that used in the flexible pipe. In all cases, coupons should be manufactured from material taken from the same manufacturing run, with baseline properties characterised. Small sample analysis techniques are available—typically, CIV measurement requires approximately 1g of material. Larger samples for mechanical testing have also been used by some operators.

The only current “active” on-line option is the FDEMS (Frequency Dependent Electro-Magnetic Sensing) sensor. FDEMS measurements can be correlated to changes in mechanical properties, such as elongation at break. It has been shown that while mechanical properties change slowly with time until relatively close to failure and have large scatter, electrical measurements change right from the start of exposure.

Details of the polymer monitoring equipment currently deployed offshore can be obtained through commercial sources.

4.2 IMPLEMENTATION OF MONITORING STRATEGY

If the monitoring strategy demands inspection of the PA-11 pressure sheath, as a result of the forecast operational conditions, the anticipated service life, and a risk assessment, it is normal to employ a combination of methods.

The selection of risers, flowlines and jumpers to be monitored and the schedule for data collection, including coupon retrieval, is made through detailed consideration of layout, design conditions, and pipe criticality, as part of the risk assessment.

It is possible to install monitoring equipment both subsea and topsides. In production systems, subsea monitoring allows direct access to the most severe operating conditions, although coupon retrieval for example is more difficult. Some effort is required to enable topside monitoring to accurately report the state of pipes throughout the system. The detailed service history of all flexible pipes is required so that their condition can be determined through appropriate ageing models. There is a need to place sample holders where they will be exposed to the most representative conditions, e.g., downstream of chemical injection points. Any differences between the pipe exposure and the coupon exposure should be considered^(11, 12).

There is also a need for accurate, reliable operational data for extrapolating topsides monitoring results to other parts of the system: temperature; pressure; pH of the produced water; % water cut; and cumulative use of production chemicals (acids, amines, alcohols, and hot oil).

Periodic review of all this data to assess the pressure sheath technical integrity should form part of the overall flexible pipe Integrity Management System⁽¹³⁾.

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APPENDIX A—DETAILED CHEMISTRY OF POLYAMIDE 11 AGEING

A.1 Introduction

The ageing of thermoplastics and the consequent loss of materials' properties are always complicated phenomena because of the superposition of several effects. Errors in the precise definition of the real life ageing conditions can easily lead to false conclusions.

In the case of PA-11 three main ageing processes have been identified for the case of ageing in oilfield flexible pipes^(1, 2, 3, 4, 5, 6):

- Structural changes due to annealing upon heating;
- Swelling by oil components and water uptake as well as plasticiser loss;
- Loss of molecular weight due to a chemical reaction with water, i.e., hydrolysis.

In oilfield flexible pipes there is an absence of oxygen, and therefore, hydrolysis is clearly established as the main mechanism for molecular weight loss. Moreover, as molecular weight goes down, the performance of PA-11 is eventually affected, in particular elongation at break or impact resistance (see also Appendix 6). There is wide experience within polymer science of the concept that material toughness is lost with decreasing molecular weight^(7, 8, 9).

A.2 Hydrolysis in Neutral Medium, Water at pH 7

The hydrolysis reaction is reversible and can be described in simplified form as follows:



In order to describe the presence of a significant reverse polycondensation reaction along with the hydrolysis reaction, it is useful to introduce an equilibrium constant which reflects the ratio of these two rates. It is defined as follows.

$$K_{eq. (T)} = \frac{[-\text{NHCO-}] \cdot [\text{H}_2\text{O}]}{[-\text{CO}_2\text{H}] \cdot [-\text{NH}_2]} = \frac{k_p}{k_h}$$

where

$[-\text{NHCO-}]$ = concentration of amide units,

$[-\text{NH}_2]$ = concentration of amine end groups,

$(-\text{CO}_2\text{HH})$ = concentration of acid end groups,

$[\text{H}_2\text{O}]$ = concentration of water,

k_p = rate constant for solid state polycondensation,

k_h = rate constant for hydrolysis.

Four assumptions are made in order to calculate the overall hydrolysis:

Where:

1. Concentration of acid and amine end groups are equal, i.e.,

$[-\text{NH}_2] = [-\text{CO}_2\text{H}]$, at the beginning of the reaction.

2. Amide concentration is constant, i.e.,

$[-\text{NHCO-}]$ = constant. This hypothesis assumes that the polymerisation level (conversion of monomer to polymer) is high at all times. Only the beginning of the conversion of the hydrolysis reaction is relevant. Example: For an initial number-average molecular weight (\overline{M}_n) of PA-11 around 30000 and a weight average molecular weight (\overline{M}_w) of 60000, there are roughly 150 amide units per chain. To reduce the molecular weight by half, it is necessary to hydrolyse one amide unit per chain. Hence, conversion is $1/150$ parts or 0.67%.

3. Concentration of water is constant, i.e.,

$[\text{H}_2\text{O}]$ = constant. This hypothesis assumes that the overall reaction is not limited by diffusion of water, and this is justified by the fact that water diffusion at a given temperature is considerably faster than hydrolysis reaction. The hypothesis is confirmed for flexible pipe pressure sheath by both analytical and experimental approaches. Literature on water absorption and water diffusion in polyamides can be found in References 11, 12, and 13.

4. The influence of plasticiser is neglected. This hypothesis is based on the fact that plasticiser does not interfere in the hydrolysis reaction - it is chemically inert. Also it does not greatly influence the overall concentrations of different species considered.

The rate equation for the reactions involved is:

$$\begin{aligned} -\frac{d[-\text{NH}_2]}{dt} &= -\frac{d[-\text{CO}_2\text{H}]}{dt} \\ &= k_q[-\text{CO}_2\text{H}][-\text{NH}_2] - k_h[-\text{NHCO-}][\text{H}_2\text{O}] \end{aligned}$$

The two opposing reactions, hydrolysis and recombination, lead to an equilibrium molecular weight being reached. A full derivation of this equation using the above approximations leads to the following equation describing the evolution of polymer molecular weight change as it decays from its initial value of \overline{M}_{w_i} to an equilibrium value \overline{M}_{w_e} as a function of time^(3, 10):

$$\overline{M}_{w_t} = \overline{M}_{w_e} \left(\frac{1 + \frac{\overline{M}_{w_i} + \overline{M}_{w_e}}{\overline{M}_{w_i} - \overline{M}_{w_e}} e^{Jt}}{1 + \frac{\overline{M}_{w_i} + \overline{M}_{w_e}}{\overline{M}_{w_i} - \overline{M}_{w_e}} e^{Jt}} \right)$$

where

$$J = 2(k_h k_p [-\text{NCHO-}][\text{H}_2\text{O}])^{0.5},$$

and

$$\overline{M}_{w_e} \propto (k_h / k_p [-\text{NHC-O}][\text{H}_2\text{O}])^{-0.25}.$$

Here, the notion of concentration must be used with care. Concentration is only well defined in homogeneous media, but solid PA-11 is not strictly homogeneous as there are amorphous and crystalline regions. The amount of crystallinity depends on thermal history but is typically 20% to 30%. As the amorphous regions largely prevail the notion of a quasi-homogeneous material is justified. Furthermore, it has been shown that PA-11 hydrolysis is random along the chain supporting the assumption that heterogeneity due to the semi-crystalline structure is not important⁽¹⁴⁾.

Further basic literature references on polyamide hydrolysis can be found in References 15, 16, 17, and 18. Literature on polycondensation or hydrolysis reactions of polyamides in the solid state can be found in References 19 and 20.

Many studies carried out in the context of defining the lifetime of PA-11 in offshore conditions have shown that the equilibrium molecular weight, \overline{M}_{n_e} , is independent of starting molecular weight, \overline{M}_{n_0} and that the rate constant J is Arrhenius activated in the temperature range 90°C to 140°C, allowing a reasonable extrapolation to lower operating temperatures^(3, 21, 22).

A simplified equation has been proposed as a working tool, to describe the molecular weight decrease linked to hydrolysis^(1, 23):

$$\eta_t = \eta_e + (\eta_i - \eta_e) \exp[-K.t]$$

where

- η_t = corrected inherent viscosity at time t ,
- η_i = corrected initial inherent viscosity,
- η_e = corrected inherent viscosity at equilibrium,
- K = constant.

It is possible to trace this equation back to the exact analytical expression if two additional assumptions are taken:

1. The molecular weight depends linearly on corrected inherent viscosity, such that:
 $\overline{M}_{n_t} = A\eta_t$, with A as constant.

Starting from well-defined Mark-Houwink equation:

$$[\eta] = K_{MH} \overline{M}_w^\alpha$$

it could be stated that such relationship could be extended quite similarly to corrected inherent viscosity in a first approximation:

$$\eta = K' \overline{M}_w^{\alpha'}.$$

A linear interpolation is valid in a well-limited molecular weight range, leading to:

$$\eta = A\overline{M}_w + B, \text{ with } A \text{ and } B \text{ as constants.}$$

However, in this case, constant B cannot be considered as negligible, and it becomes difficult to validate the assumption described above.

2. The following expression holds: $\frac{\eta_e + \eta}{\eta_e + \eta_i} = 1$

This is only valid when the range of viscosities analysed is close to the initial viscosity.

As a consequence, the empirical equation described above cannot be rigorously justified. However, the equation fits well experimental data, and can be used as a first order approximation and simple mathematical working tool.

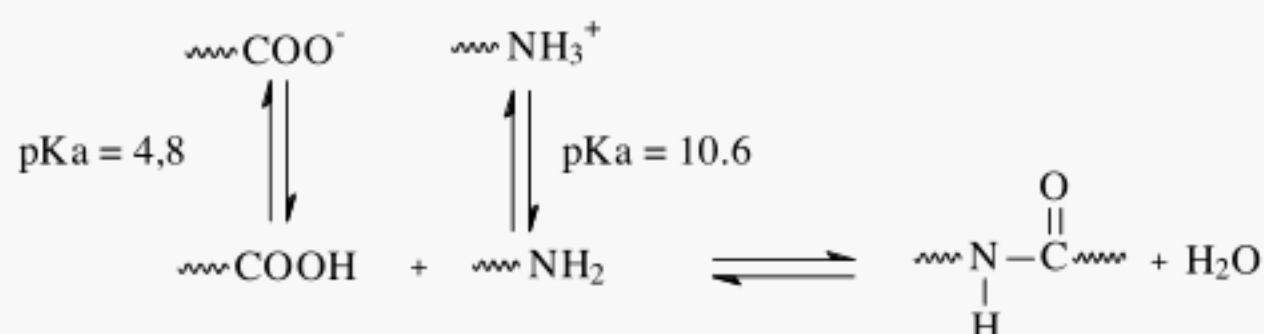
A.3 The Role of Acids During Hydrolysis

In the ageing of flexible pipes, acids present in produced oil and gas play an important role. These acids are mainly carbonic acid and hydrogen sulphide, and to a lesser degree organic acids present in oil and characterised by the Total Acid Number, TAN.

As stated earlier, acids can accelerate hydrolysis^(24, 25, 26, 27, 28, 30). It has been shown that they only have a catalytic effect when their concentration exceeds that of the amine end-group⁽²⁹⁾. Therefore, a precise knowledge of their effect

in offshore oil and gas production conditions is important to estimate the lifetime of the PA-11. First detailed studies on acid degradation of PA-11 are given in References 31 and 32.

The overall reaction is as follows:



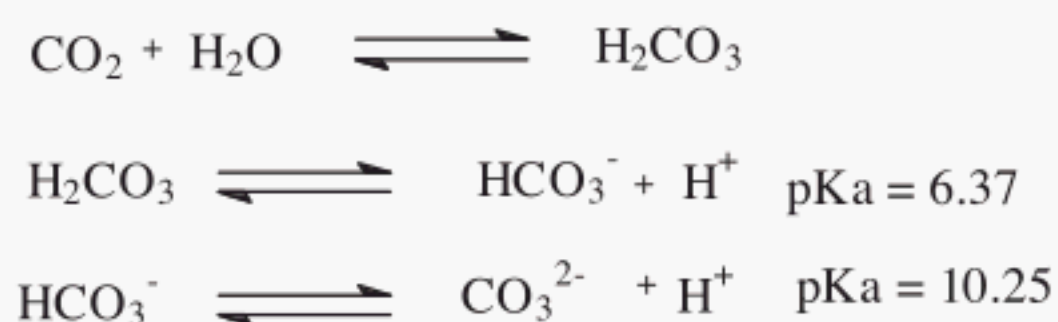
By calculation, in water at pH 7, 99.97 % of amine end groups exist as ionic species (protonated form) and 99.37% of acid end groups exist as ionic species (deprotonated form). If then, for example, an acid of pH 4 is added, the deprotonated carboxylate species, ---COO^- , is reduced to 13.68%, and the ammonium species, ---NH_3^+ , is increased to 99.99997%. This is important because the amine function, ---NH_2 , is decisive for the polycondensation reaction—it is the nucleophilic species capable of forming the chemical bond with the carboxylate group.

Therefore, the presence of acidity (with pH going from 7 to 4, for example) induces a very large decrease of the concentration of chemically active species in polycondensation, ---NH_2 , by three orders of magnitude (3×10^{-2} to 3×10^{-5}).

This decrease can also be considered as amine functions being eliminated from participation to the polycondensation equilibrium, as they become protonated. In chemical terms, this is amine scavenging linked to the presence of acids.

A.4 Acidity Created by Carbon Dioxide

The presence of carbon dioxide and water creates carbonic acid:

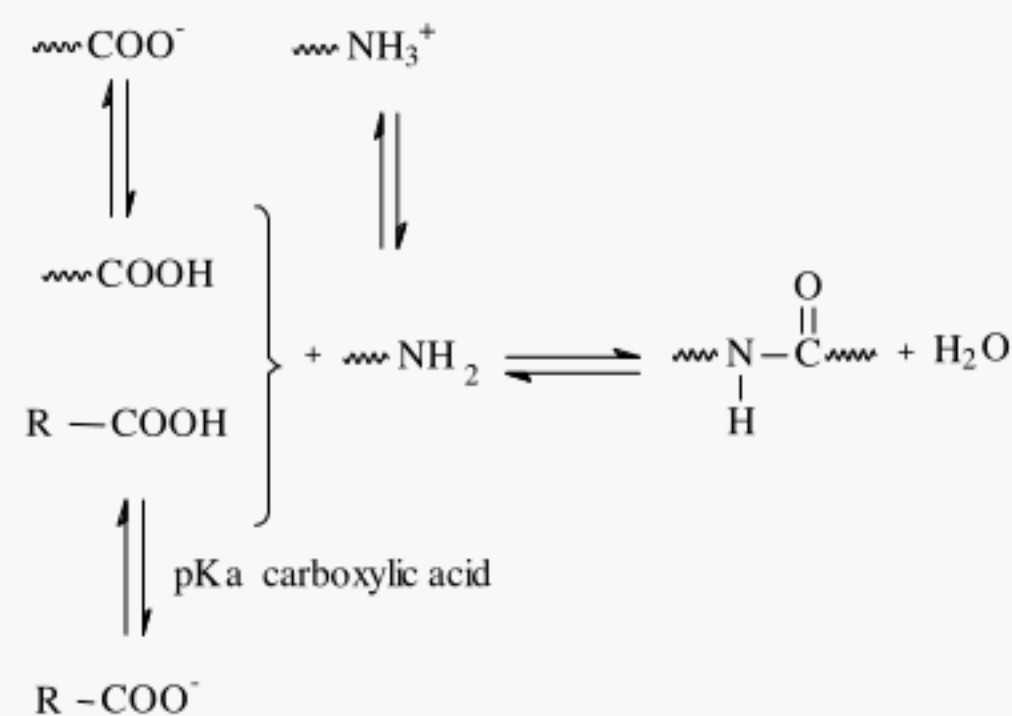


The amount of carbon dioxide dissolved and generating the acidity depends directly on pressure^(37, 38). It is therefore anticipated that the decrease of molecular weight due to CO_2 depends directly on its partial pressure.

Experimental evidence has confirmed that PA-11 molecular weight decreases in the presence of CO_2 . There are also indications from laboratory testing and field experience that hydrolysis in the gas phase of CO_2 and water is slower than the liquid water phase. This is as yet unexplained by theory.

A.5 The Effect of Organic Acids Present in Oil

In the case of carboxylic acids present in crude, consideration must be given to the acidity (increase in proton concentration) due to the acid addition—as discussed above—and, also to the carboxylic acid participating as an “acid end group” in the equilibrium polycondensation / hydrolysis reaction, according to the following scheme:

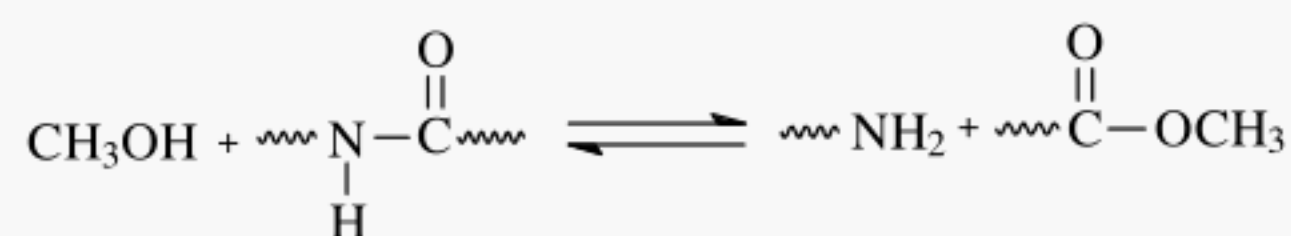


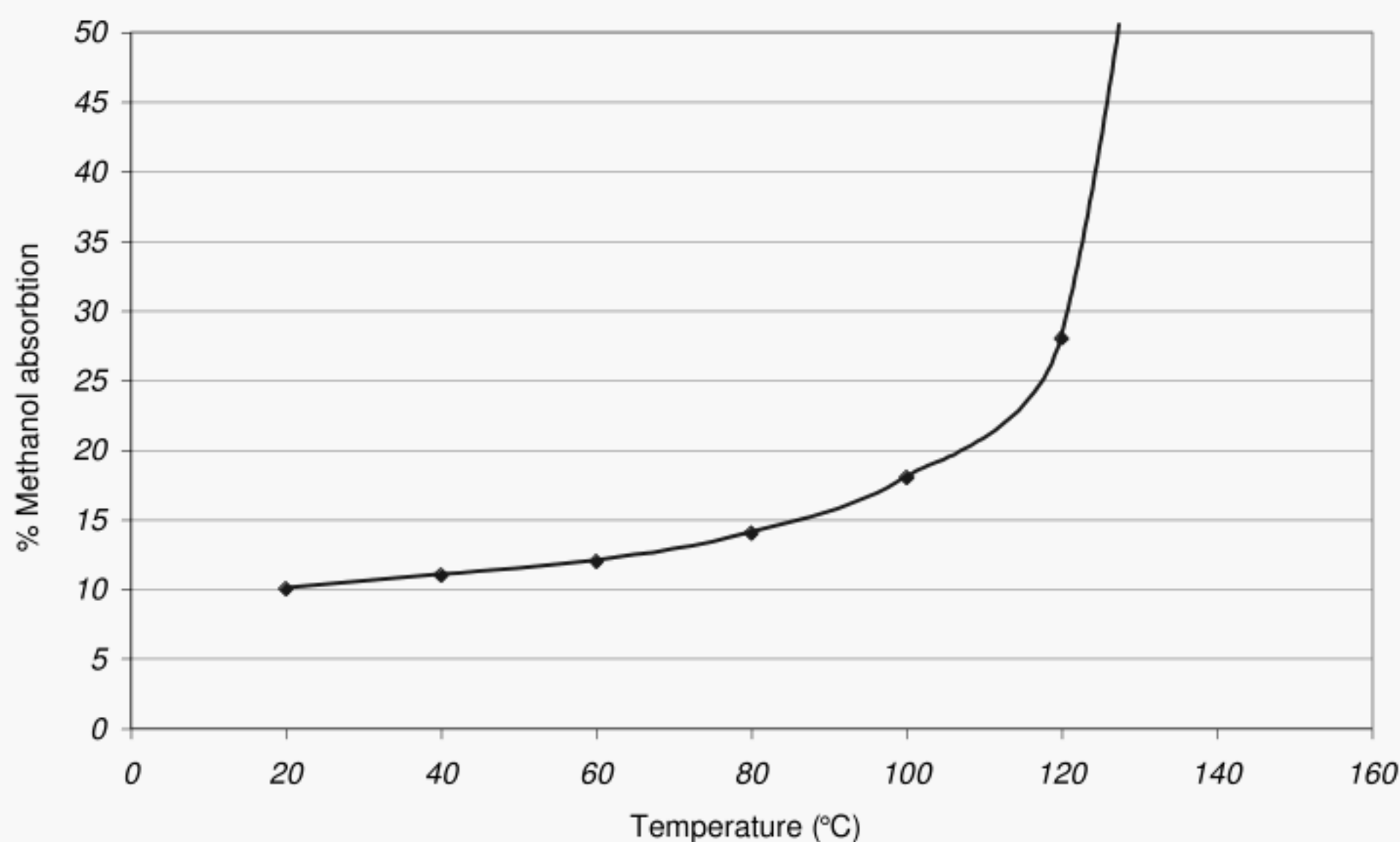
In the case of carboxylic acids, interaction of acid species with PA-11 necessitates the diffusion of large molecules into the polymer layer. This diffusion can be considerably slower, depending on nature and size of considered acid, than the diffusion of water or CO_2 ⁽³³⁾. Therefore, a gradient of hydrolysis reaction across the sample thickness can be observed. Some samples retrieved from the field have shown this “skin effect.”

The action of carboxylic acids participating as “acid end groups” in polycondensation/hydrolysis reactions, and the reduced diffusion rate of large acid molecules in PA-11 have been illustrated by a case study where PA-11 was aged with phthalic acid buffer⁽³⁴⁾. In this case, incorporation of carboxylic acid into PA-11 as chain end group was proven by analytical methods (FTIR, NMR, MALDI-TOF mass spectroscopy). In the case of phthalic acid, the resulting imide species can be easily differentiated from amide functions, and imide bond concentration as a function of sample thickness clearly revealed the presence of a “skin effect” due to the limited acid diffusion rate through the polymer.

A.6 Ageing Due to Methanol

Chemical reaction of PA-11 with methanol is rather similar to hydrolysis, i.e., “methanolysis”:





The presence of methoxy end groups, in the same amount as amine end groups, correlated with the absence of acid end groups in the PA-11 after reaction with methanol, has been fully confirmed by ^{13}C , ^1H NMR, and FTIR analyses⁽³⁵⁾.

The concentration of methanol absorbed by PA-11 under saturation conditions is much higher than the amount of water absorbed at saturation. This explains why the extent of molecular weight decrease can be more than for water. Moreover, the amount of methanol absorbed in the PA-11 under saturation conditions is much more temperature dependent than for water. Methanol absorption of BESNO P40 grades is illustrated in the above graph⁽³⁶⁾.

This “quasi-solvent” behaviour at high temperature (such as 120°C) induces modifications of the polyamide morphology which have a much more pronounced influence on material properties than molecular weight loss. Extrapolation of high temperature ageing results to actual service conditions is, therefore, not ideal.

Experimental studies and field experience confirm that PA-11 can be used in the presence of methanol at a temperature of 60°C for many years. In addition, the conditions of pure methanol ageing or diluted methanol ageing are very different, the induced swelling by diluted methanol being much reduced.

A.7 Oxidation

Oxidation is primarily of concern in laboratory ageing tests rather than in the field. No noticeable oxidation phenomena take place in the field, degradation being linked only to hydrolysis.

In order to get valid data from laboratory testing to model PA-11 behaviour under oilfield conditions, it is of primary

importance to perform experimental tests in conditions as close as possible to the field. Appendix B contains guidance as to how to exclude oxygen from laboratory tests, a fundamental precaution during any laboratory study devoted to PA-11 ageing in oilfield conditions.

If no special care is taken during laboratory ageing tests, oxidative degradation can easily occur, and results of such tests are of little use for oilfield applications. The use of higher temperatures in laboratory tests to accelerate ageing reactions, in order to reduce experiment times, also contributes to emphasise the potential influence of thermo-oxidation processes.

Experience shows that the presence of oxygen during PA-11 ageing leads to specific consequences:

1. Rapid PA-11 coloration, yellow, then brown. In the absence of oxygen, samples remain white.
2. Typically, lower molecular weight values. This effect is specifically noticeable for long ageing times (corresponding to the equilibrium plateau).
3. A major influence on mechanical properties, such as elongation at break, after PA-11 ageing, even in pure demineralised water.
4. Creation of artefacts in crude oil experiments. Oxygen reacts with crude oil during ageing to create organic acids, with considerable negative consequences. Even proper oxygen removal procedures may be insufficient to completely avoid residual traces generating artefacts for long ageing times at high temperatures. This means that performing valuable laboratory tests with crude oil is much more difficult than with pure water.

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APPENDIX B—GUIDANCE ON LABORATORY EXPOSURE TESTING

B.1 General

This Appendix contains general guidance on the proper way to carry out ageing experiments to simulate oilfield environments, capturing the learning of the last few years.

B.2 Oxidation

Oxidation is primarily of concern in laboratory ageing tests rather than in the field. If no special care is observed during laboratory ageing tests, two different degradation mechanisms will be present, and oxidative degradation will occur in addition to the hydrolysis. The use of higher temperature in laboratory testing than in real service conditions (in order to reduce experiment times) can also contribute to emphasise the influence of oxidation processes.

As a result, a proper oxygen removal procedure is required for any laboratory study devoted to PA-11 ageing in field conditions.

To ensure the absence of oxygen in ageing experiments, high purity nitrogen or argon (> 99.999%) should be bubbled through the solution until the residual oxygen in the outlet gas is < 10 ppm.

Even with proper fluid replacement and oxygen removal procedures, performed at each sampling time, some very low residual amounts of oxygen are nevertheless present after nitrogen bubbling. This results in conservative ageing data.

Any gas used as the ageing environment should likewise have oxygen content < 10 ppm.

B.3 Open or Closed System

Another difficulty concerning the relation between laboratory and field conditions is linked to the flowing service encountered in the field compared to the static conditions mostly employed in laboratory tests.

False interpretation can result from species either accumulated or exhausted as a direct consequence of the closed, static laboratory environment, e.g., when experiments are carried out with an ageing medium comprising only limited percentage of particularly “active” species for PA-11 degradation, such as water with acids, or oil with well-defined TAN. It is then of primary importance to consider carefully the ratio between the available amount of such chemicals and polyamide in contact. Indeed, if the medium is not regularly renewed, exhaustion of the concerned species will occur, and polymer degradation will be slowed down—and ultimately stopped—exclusively due to laboratory test conditions.

It should be noted that the rate of plasticiser loss can be affected by regular change-out of water, due to limited solubility of plasticiser in water.

B.4 Single-sided Versus Multiple-sided Sample Exposure

Single-sided versus multiple-sided sample exposure constitutes another difference between real service and laboratory test conditions. Single-sided sample exposure represents real ageing conditions, but is rarely reproduced in laboratory tests. This is rarely a real issue in laboratory experiments which are primarily designed to determine or confirm ageing rates.

B.5 Sample Preparation for Mechanical Testing

Tensile testing is often performed to characterise the mechanical properties of aged PA-11. In such cases, sample preparation has an important influence on the results.

Different sample preparation methods can be considered: ageing of a tensile specimen punched out from virgin extruded sheet; ageing of an extruded sheet before punching out the tensile sample; ageing of an injection moulded sample; or ageing of tensile specimens machined from extruded pressure sheath. The sample preparation induces differences in surface roughness and crystallinity, and therefore in the results of mechanical tests carried out after ageing, particularly elongation at break, without any effect on the molecular weight.

It is preferable to use extruded pressure sheath samples in order to adequately represent the mechanical behaviour of aged pipes in offshore conditions.

B.6 Simulating Acidic Conditions in the Laboratory

It must be recognised that different methods of attaining pH will affect ageing kinetics.

The effect of CO₂ should be directly simulated using CO₂. Organic acids or buffered acids, sometimes used in laboratory testing because they offer constant pH in any water phase, should be avoided.

B.7 Use of High Temperature for Laboratory Tests—Modification of Morphology

Laboratory experiments are often performed at higher temperature than in service, in order to accelerate ageing to a convenient time scale. However, if a chosen temperature is too high, high temperature annealing processes may come into play, inducing substantial modification of microstructure and morphology, i.e., a lamellae consolidation effect. Such effects are an artefact of the high temperature and may not occur at lower temperature. The temperature of 140°C appears to be

the upper temperature limit for performing useful ageing tests on PA-11 samples.

The presence of *methanol* greatly magnifies the consequences of high temperature during laboratory experiments. Methanol solubility in PA-11 greatly depends on temperature, especially above 90°C, and methanol becomes a solvent of polyamide at 140°C. Therefore, experiments performed in pure methanol at high temperature (such as 120°C for example) are in fact carried out in “quasi-solvent” conditions. It

has been observed that polymer structure (crystalline level and morphology) is hugely modified by such “quasi-solvent” interactions. Methanol ageing data obtained at temperatures above 90°C cannot be extrapolated to lower temperature.

High temperature (>120°C) ageing of PA-11 with ethylene glycols can lead to the formation of acidic degradation products in the fluid. This makes interpretation of such high temperature tests difficult.

APPENDIX C—COMPARISON OF MOLECULAR WEIGHT DETERMINATION TECHNIQUES

C.1 General

There are many different possible methods to measure polymer molecular weight, each with advantages and drawbacks. In the general case of polyamides, very limited solubility is an important factor making molecular weight determination a difficult task compared to many other polymers. However, an abundant literature exists and molecular weight determination of polyamides can be considered as standard today, though not necessarily “easy”^(1–12). The following methods are of interest:

- a. *End group analysis*, i.e., titration of amine or acid end groups, is a very useful method for the molecular weight characterisation of polyamides. It counts the total number of chains in a very direct manner and is thus sensitive to the “number-average molecular weight.” However, as the number of end groups is inversely proportional to the molecular weight, the method becomes limited for higher molecular weights. Experience shows that precision drops drastically at number-average molecular weights above 10000. Another drawback is the possibility of end group modification during ageing. This method is not recommended for analysis of flexible pipe components.
- b. *Colligative methods*, such as cryoscopy or vapour pressure osmometry, are based on thermodynamic principles (melting point depression or vapour pressure depression). They are sensitive to the number of molecules dissolved and hence allow the measurement of the “number-average molecular weight.” The methods have not gained acceptance for polyamides, mainly due to lengthy procedures and a lack of standardised equipment. The often aggressive (corrosive, toxic) character of polyamide solvents necessitates specialised equipment. In principle, these methods are powerful and give absolute molecular weight data, but there is very little data and experience available today.
- c. *Solution viscosity* methods are based on the increase of viscosity of a given solvent due to the presence of dissolved polymer chains. The method is therefore sensitive to the hydrodynamic volume of the dissolved polymer chains which can be correlated with the “viscosity-average molecular weight.” It has been shown in numerous literature reports that this value is nearly equivalent to the “weight-average molecular weight.” The detailed theoretical basis for this method is described in detail in Appendix D.

Well-established methods have been defined in an intermediate dilute regime, measuring “inherent viscosity” values, which can be well correlated to the molecular weight. In order to have a good correlation between viscosity measurement and polymer molecular weight on an aged plasticised material, it is necessary to take in account the polymer fraction in the analysed sample. It is therefore necessary to measure the

amount of non-polymeric species present in the sample, leading to so-called “corrected inherent viscosity” values. The assumption is made that these impurities do not significantly affect the viscosity behaviour of PA-11 solutions.

It is important to note viscosity gives relative measure of the change in Molecular Weight based on the solvent and temperature usage. It does not provide an absolute measure of molecular weight. The solution viscosity can be converted to molecular weight, and vice versa, using the Mark-Houwink equation, described in Appendix D. It is a robust method which is readily standardised and is reproducible in different laboratories.

d. *Size exclusion chromatography (SEC) or gel permeation chromatography (GPC)* is based on the hydrodynamic volume of dissolved polymer chains in solution and the time lag particles show when they pass through a porous substrate. It has been shown that larger particles do not penetrate through smaller pores and thus traverse more quickly the stationary porous substrate than smaller particles which have much longer path-lengths.

Direct access to absolute molecular weight is not intrinsic to the SEC method, but depends on the output detector used and / or the calibration of the molecular weight using polymer standards. By connecting a multi-angle laser light scattering (MALLS) detector to a GPC/SEC system, the absolute molar mass and size distributions of a sample can be determined directly, without resorting to calibration techniques or making assumptions about a sample’s conformation. The SEC-MALLS instruments allow the molar mass and size distribution to be calculated.

Different parameters such as the treatment of baselines and the choice of integration boundaries have extensive effects on the values obtained. Moreover, due to the aggressiveness of common polyamide solvents, care has to be taken about the progressive deterioration of the porous stationary phase. Minor changes in solvent quality can also have strong effects on the measurement. An adequate use of this technique requires the use of “master samples.” Daily or regular analysis of such reference samples provides adequate validation of the performed measurements.

The major advantage of SEC method is that it allows to fractionation of the polymer according to the chain length and access to the molecular weight distribution. From this distribution, different molecular weight averages (\overline{M}_n , \overline{M}_w , \overline{M}_z) can be calculated. As a standard method, this method is probably too complex.

In order to compare CIV and SEC-MALLS measurements, it is necessary to use the so-called Kramer and Mark-Houwink relationships. Industry consensus on the constants required for PA-11 within these relationships is currently being urgently sought. CIV of 1.80 dl/g is thought to correspond to \overline{M}_w in the range 60000 to 70000 g/mol, 1.20 dl/g to \overline{M}_w 25000 to 35000

g/mol; and 1.05 dl/g to \overline{M}_w 22500 to 27500 g/mol. Reports of molecular weight measurements should always state whether values are measured or calculated. If calculated, a full list of constants used should be included.

C.2 Conclusions

Of the methods available to quantify the molecular weight characteristics of PA-11, solution viscosity is a good standard method. It is widely used, simple to perform, easily automated and has a good chance to being reproducible in different laboratories. It provides a relative average of the molecular weight and does not provide a full description of the molecular weight distribution. Knowledge of the full molecular weight distribution is not crucial in an hydrolysis experiment as it generally remains unchanged.

SEC-MALLS is an additional method for molecular weight determination, which has potential to be useful in flexible pipe applications. Industry consensus regarding the application of this technique for routine assessment of PA-11 life has not yet been reached. Fundamental work to establish this as a standard method is on-going, as is determination of the mathematical relationship between the various measures of PA-11 molecular weight.

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APPENDIX D—RECOMMENDED PRACTICE FOR VISCOSITY MEASUREMENT OF AGED AND FRESH POLYAMIDE 11 IN M-CRESOL

D.1 General

D.1.1 SCOPE

This procedure describes a method for measurement of the dilute solution viscosity of plasticised Polyamide11 (PA-11, RilsanTM) in meta-cresol. The calculated corrected inherent viscosity gives information about the degree of degradation of the polyamide and thus can be used to determine the remaining service life of the material.

It should be noted that the viscosity of polymer solutions can be affected by the presence of additives and absorbed species in the sample, including but not limited to colorants, fillers, plasticisers or low-molecular weight species. It is important with PA-11 to check what the absorbed or added species may be, and establish good methods to quantify them.

Also, it must be known that the polymers used to establish the correlations and those to which they are applied does not consist of or contain branched species. Severely aged PA-11 may contain branches.

One should notice that the use of gravity type capillary viscometers is limited to polymer solutions that do not deviate much from Newtonian behaviour.

The procedure does not describe the safety concerns (if any) connected with its use.

D.1.2 NORMATIVE STANDARDS AND PROCEDURES

API

- RP 63 *Recommended Practices for Evaluation of Polymers used in Enhanced Oil Recovery Operations*, Section 3, "Polymer Solution Rheology and Flow Through Porous Media."

ASTM¹

- D2857-95 *Standard Practice for Dilute Solution Viscosity of Polymers*. Relative viscosity determined by this practice is not equivalent to those determined by ASTM D789.

ISO²

- 307:1994 *Plastics—Polyamides—Determination of viscosity number*.
- 1628/1 *Guidelines for the Standardization of Methods for the Determination of Viscosity*

¹American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428.

²International Organization for Standardization, 1 Rue de Varembé, Case Postale 56, CH 1211 Geneva 20, Switzerland.

Number and Limiting Viscosity Number of Polymers in Dilute Solution.

3105 *Glass capillary kinematic viscometers: Specifications and operating instructions.*

6427-1982(E) *Plastics—Determination of matter extractable by organic solvents (conventional methods).*

DIN³

51562-2 *Viscometry: Determination of kinematic viscosity using Ubbelohde microviscometer (1988).*

ATOFINA Procedure MOD-LEM/ANACHIM-039 (12/11/96) *Determination de la Viscosite des Polymeres en Solution.*

Coflexip Ref.04DEET104 *Viscosity test of polyamides in solution.*

Kranbuehl Lab. JIP Procedure for the Characterisation of the ageing of Polymers in an Oil-Gas-Offshore Environment (Dec. 4, 1997). IV *Intrinsic Viscosity Sample Measurement and Viscometer Cleaning.*

US Patent 5,614,683: *Method and apparatus for monitoring nylon 11 made from polyamide plastic made from aminoundecanoic acid.*

Measuring temperature in this procedure is set to 20°C due to practical and historical reasons. ASTM D2857-95 uses 30°C while Kranbuehl lab. and ISO 1628/1 and 307 recommends 25°C.

D.1.3 REFERENCES

Fred W. Billmeyer, Jr.; *Textbook of Polymer Science*, John Wiley & sons. 1984.

R. Lapasin and S. Prich, "Rheology of Industrial Polysaccharides," Blackie Academic & Professional, 1995.

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D.2 Definitions

Determination of the dilute solution viscosity of a polymer is one method that can provide information about polymer chain degradation. The viscosity of a polymer solution is related to the size and extension of the polymer molecules in that particular solvent. Generally, the larger the molecules are, the higher the solution viscosity will be. Since the method is basically a measure of size, and not weight of the polymer, a correlation between the two must exist. Such a correlation is well established for many polymers in a particular solvent and at a given temperature, (Mark-Houwink's

³DIN Deutsches Institut für Normung e.V., 10772 Berlin.

Table D-1

Common name	Also known as	Symbol and Defining Equation
Relative viscosity	Viscosity ratio	$\eta_r = \eta/\eta_0 \equiv t/t_0$
Specific viscosity	—	$\eta_{sp} = \eta_r - 1 = (\eta - \eta_0)/\eta_0 \equiv (t - t_0)/t_0$
Reduced viscosity	Viscosity number	$\eta_{red} = \eta_{sp}/c$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = (\ln \eta_r)/c$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = (\eta_{sp}/c)_{c=0} = [(\ln \eta_r)/c]_{c=0}$

η = viscosity (mPas)

η_0 = viscosity of the solvent (mPas)

t = efflux time of polymer solution (seconds)

t_0 = efflux time of the solvent (seconds)

c = polymer concentration (g/cm³)

equation, see below). This is the case for linear, flexible polymers, but not for most branched polymers. The Mark-Houwink relations are tabulated in for instance Polymer Handbook (Brandrup and Immergut). A number of quantities are related to viscosity; these include the relative viscosity, specific viscosity, reduced viscosity and inherent viscosity (see below for definitions).

All these quantities are related to the polymer concentration in solution. Therefore, the intrinsic viscosity (which is independent of concentration) is a more fundamental quantity for determination of molecular weight. The intrinsic viscosity is the limit of the reduced (or inherent) viscosity as the concentration of polymers in solution goes to zero. That is, we operate in the dilute regime, and often at a low fixed shear rate. For more information see for instance ASTM D 2857-95 or Lapasin and Priel (1995).

Nomenclature of Solution Viscosity [from Billmeyer (1984)] is given in Table D.1.

In the equation defining the relative viscosity, the efflux times obtained from measuring with a capillary viscometer is used. This approximation is valid if the kinetic energy correction is negligible and the densities for the solutions with and without polymer are substantially equal (see ASTM D 2857-95).

The relationship between the specific viscosity and concentration is given by Huggins equation (1), extrapolation to infinite dilution (and also at low shear rate);

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c \quad (1)$$

where k' (Huggins constant) is a constant for a series of polymers of different molecular weights in a given solvent.

Alternatively the relationship between inherent viscosity and concentration is given by Kraemers equation (2):

$$\ln \eta_r/c = [\eta] + k'' [\eta]^2 c \quad (2)$$

where

$$k' - k'' = 0.5, k'' = \text{Kraemers constant.}$$

Note: Inherent viscosity equals the intrinsic viscosity only at low concentrations, but since Kraemers constant is usually low, inherent viscosity at a low concentration (0.5 g/dl for polyamide 11) can be an approximate measure of intrinsic viscosity and therefore also the polymer chain length.

All the above considerations hold for neutral polymers. Polyamide 11 has charged chain ends and protonated amide groups in solution. If such a solution is diluted the degree of ionic association between the polymer and its counter ions becomes smaller. This causes an increase of the polymers effective net charge, which again causes an expansion of the polymer and therefore also an increase in viscosity. The expansion of the polymer with dilution can be eliminated if the ionic strength is kept constant during dilution. In the case of polyamide we measure at a polymer concentration which is high enough to eliminate this so-called electro viscous effect. On the other hand, the concentration should not be high enough for the polymer chains to overlap. This overlap concentration can, as a rule of thumb, be approximated as one over the intrinsic viscosity. For polyamide 11, intrinsic viscosities in the range 1 to 2 dl/g, are common. This corresponds to overlap concentrations from 0.5 to 1 g/dl. Experience has shown that measuring at 0.5 g/dl is a compromise that accounts for all the effects mentioned above.

The Mark-Houwink equation describing the relation between intrinsic viscosity and molecular weight is given by:

$$[\eta] = KM^a \quad (3)$$

where

the parameters K , and a , depend on the particular polymer-solvent pair and on the temperature, and M the polymer molecular weight.

Note: The Mark-Houwink equation gives a relationship between intrinsic viscosity and the absolute molecular weight of a monodisperse polymer. Since most polymers are polydisperse, applying equation 3 gives a molecular weight (M) that is a so-called viscosity average molecular weight. The value of M lies between the number and weight average molecular weight. Generally, M is much closer to the weight average molecular weight than the number average molecular weight, and with $a = 1$ in Mark-Houwink's equation, they are equal.

D.3 PA-11 Material Storage and Handling

RilsanTM contains additives (10 – 12 wt %), and absorbs water and other solvents. Care must be taken when retrieving, handling, transporting and storing samples from laboratory ageing or field service, or long time storage of fresh reference samples.

To ensure that RilsanTM samples does not change before characterisation, it is recommended to store under dry, dark and cool (below 20°C) conditions. Irradiation may also change the material.

For viscosity measurements: Sealed plastic bags, in refrigerator or at room temperature.

For measurement of extractables: Wrap the samples in Al-foil, and keep them in sealed plastic bags, preferably in a refrigerator until measurement.

D.4 Apparatus, Reagents and Materials

This procedure refers to ISO 307:1994, with 20°C in the bath instead of 25°C.

D.4.1 APPARATUS

- Vacuum drying cabinet.
- Constant temperature bath at 20°C \pm 0.1°C, oil bath or water bath.
- Volumetric flask, capacity 50 ml, fitted with a ground glass stopper.
- Shaking apparatus or magnetic stirrer.
- Viscometer, glass capillary type with efflux times in the appropriate range. For instance Ubbelohde or micro-Ubbelohde for robotic systems, type capillaries (SCHOTT 538-23 ($K = 0.3$) or SCHOTT 538 ($K = 0.174$), or equivalent), see ISO 307, ISO 3105 or DIN 51562 part 2. In order to get reliable results, the efflux time of the solvent and the solution should be similar, and typically in the range of 1 to 20 minutes for the current procedure.
- Suction or pump for transfer of solution.
- Timer (0.1 s or better).
- Balance, accurate to 0.1 mg.

- Glass sinter filters (pore size between 40 μ m and 100 μ m)

Dried glassware should not be used the next day if not stored under very dry conditions.

D.4.2 POLYAMIDE

Solid, powder, PEBAX or granulated RilsanTM may be analysed with this method.

D.4.3 REAGENTS

Use only reagents of recognised analytical grade and only distilled water or water of equivalent purity. m-cresol shall be stored in a brown glass bottle.

m-cresol; meeting the specifications of ISO 307:

m-cresol content: 99 % (m/m) min.

o-cresol content: 0.3 % (m/m) max.

water content: 0.13 (m/m) max.

m-cresol of the required purity can also be obtained by distillation of chemically pure m-cresol.

Alcohol or acetone for cleaning.

Chromic acid solution for cleaning, according to ISO 307.

D.5 Preparation of Test Samples

D.5.1 REMOVING THE HIGH MW TAIL AFTER EXTRUSION

Freshly extruded pressure sheath has a high molecular weight component in the MW distribution, which is not part of a regular polycondensation molecular weight distribution with a polydispersity of 2. This high molecular weight component is immediately hydrolysed and does not contribute to the working life of the polymer.

In order to define the starting molecular weight it is preferable to eliminate this component. This is done by exposing the sample to deoxygenated water (pH = 7) for 24 hours at 80°C, for sample thickness less than 5mm.

D.5.2 SOLUTION OF M-CRESOL AND PA-11

According to ISO 307, the material is checked for extractables before weighing in the material, to ensure correct in weight of the polymer. With this procedure, the sample is weighed in as it is (only dried/dehydrated), and the corrected viscosity is calculated afterwards.

Cut thin strips of plastic without any dust. In order to dehydrate the material (less than 0.1 % water); place the material in a vacuum oven at 80°C over night.

For aged samples, separate analysis of the surface layers and inside material may be necessary to check on surface effects by non-absorbed species. A slice of 0.5 mm (or other specified thickness) is cut from the inner surface (very thin

samples may cause plasticizer to diffuse during drying). An additional 1-2 samples from the middle of the cross section and one sample from the outer surface. Dehydrate as described above.

After this time, put samples to cool during 15 minutes in a drier/desiccator.

The concentration is $5 \pm 0.02 \times 10^{-3} \text{ g/cm}^3$. Weighing must be done rapidly to minimise moisture pick-up (less than 2 min).

Then, with a density for m-cresol of 1.034, we have:

$$C = m/v = (m*d)/M = (1.034*m)/M$$

m = weight of the polyamide (grams)

M = weight of m-cresol (grams)

Prepare about 30 cm^3 of m-cresol in a graduated test tube. Pour 30 g of m-cresol into an Erlenmeyer flask (250 cm^3). Weigh 0.145 g of polyamide to obtain a concentration of $5 \pm 0.02 \times 10^{-3} \text{ g/cm}^3$.

Add the polyamide into the Erlenmeyer flask and heat it for 60 minutes at 100°C with stirring. Check visually that the dissolution is OK.

After dissolving the polymer do not wait more than 24 hours before measuring.

D.6 Procedure

The principle of the measurement is to determine the time of flow of a polyamide solution and of pure solvent (m-cresol) manually (or automatically) in a calibrated tube. The procedure used for a robotic system may be slightly different.

D.6.1 DETERMINATION OF THE FLOW TIME FOR M-CRESOL

All the glassware (Erlenmeyer, viscosity tube and graduated test tube) is washed with alcohol or acetone before drying in oven at 80°C for 30 minutes. Make sure all the glassware is completely dry before use.

Put the thermostatic bath at a temperature of $20^\circ\text{C} \pm 0.1$.

Pour a volume of 30 cm^3 of m-cresol in a graduated test tube, and then repour it through a glass sinter filter in the viscosimetric tube to a level between the two marks of the tank.

Wait about 30 minutes with the tube in the bath in order to reach the correct temperature in the m-cresol.

Bring the liquid above the upper graduation mark by suction or pumping.

When the liquid reaches a level slightly higher than the upper graduation mark the tube is put under atmospheric pressure, which allows the liquid to flow down. To measure the efflux time, start the timer exactly as the meniscus passes

the upper graduation mark, and stop it exactly as the meniscus passes the lower mark.

The test result is valid as soon as three successive values agree within 0.5 %.

D.6.2 MEASUREMENT OF FLOW TIME OF SOLUTION

Put the bath at a temperature of $20^\circ\text{C} \pm 0.1^\circ\text{C}$.

Pour a volume of 30 cm^3 of the solution in a graduated test tube, and then repour it through a glass sinter filter in the viscosimetric tube to a level between the two marks of the tank.

Wait about 30 minutes with the tube in the bath in order to reach the correct temperature in the solution.

Bring the liquid above the upper graduation mark by suction or pumping.

When the liquid reaches a level slightly higher than the upper graduation mark, the tube is put under atmospheric pressure, which allows the liquid to flow down. To measure the efflux time, start the timer exactly as the meniscus passes the upper graduation mark, and stop it exactly as the meniscus passes the lower mark.

The test result is valid as soon as three successive values agree within 0.5 %.

With each sample, carry out at least two determinations of the inherent viscosity, each time using a fresh solution, until two successive values meet the repeatability requirement (better than 3%).

After finishing the measurements on the polymer solutions, another measurement on pure m-cresol should be done and the resulting efflux time compared with the efflux time obtained from the first measurements.

D.6.3 CLEANING PROCEDURE

No cleaning necessary between measurements performed on the same solution.

Between measurements on different solutions, rinse with acetone or alcohol. Dry in oven or with air.

If removal of dust or dirt is necessary, fill the viscometer with chromic acid solution, and leave it over night. Rinse with water, then clean with alcohol or acetone.

The procedure used for a robotic system may be slightly different.

D.7 Procedures for Determination of Extractables in PA-11

Several methods may be used to determine the extractable content of the material. Only one method is referred to in this procedure, that is the Atofina procedure. More work needs to be done on verification of alternative methods (TGA, SFE, extraction etc.).

D.7.1 BY VACUUM AND ELEVATED TEMPERATURE (ATOFINA PROCEDURE)

Extraction/evaporation during more than 90 minutes at 230°C in an oven at < 0.1 mbar vacuum, measured at the pump. Record the total weight loss of the material.

Make sure this procedure is done on predried samples, identical to the samples weighed into solution. At least two parallels should be run on each sample (should be within 10%).

D.8 Viscosity Calculations

D.8.1 INHERENT VISCOSITY (LOGARITHMIC VISCOSITY NUMBER)

Calculate the inherent viscosity ratio for each solution concentration as follows:

$$\begin{aligned}\text{Inherent viscosity (cm}^3/\text{g)} &= \ln(t/t_0) \times 1/c \\ &= \ln(t/t_0) \times M / (1.034 \times m) \times 10^{-2} \\ &= \log(t/t_0) \times 2.30/c\end{aligned}$$

where

- t_0 = flow time for m-cresol (seconds),
- t = flow time of the solution (seconds),
- M = weight of m-cresol solution (g),
- m = weight of the polyamide (g),
- c = concentration g/cm³.

D.8.2 CORRECTED INHERENT VISCOSITY

Corrected inherent viscosity is achieved by recalculating with the correct polymer in-weight:

$$(\text{corrected viscosity}) = (\text{uncorrected viscosity}) * (100 / (100 - \text{Extractable}))$$

Extractable content is expressed in % by weight.

D.9 Report

Report the following information:

- Complete identification of the sample
- Exposure conditions if aged
- Date of retrieval and measurement
- Weight change since retrieval
- Changes in color or appearance
- Solvent
- Precipitation in solution
- Bath temperature
- Concentration of the test solution
- Weight before and after dehydration
- Extractables, weight before and after vacuum extraction
- Measured inherent viscosity in dl/g
- Measured efflux times
- Corrected inherent viscosity in dl/g (with standard deviation)
- Description of equipment
- Sampling method
- Reference to this procedure

D.10 Precision, Sources of Uncertainty

The Atofina procedure gives the inherent viscosity result with ± 0.02 dl/g.

ISO 307-1994 reports a repeatability of 3% and a reproducibility of 10 % for m-cresol solutions (results from a Round Robin in 1982).

An assessment of other possible sources of deviation in the results is necessary; some of the possible factors are listed below (from ISO R1628-1970):

- Surface tension
- Capillary end effect
- Drainage effect
- Viscous heat effect
- Deviation of the viscometer from the vertical
- Hydrostatic head variations
- Losses by evaporation
- Errors in concentration and efflux time
- Shear effect
- Errors in temperature stability and measurement
- Kinetic energy

APPENDIX E—SUMMARY OF ROUND ROBIN RESULTS

E.1 Background

During 1999 work was initiated within the RilsanTM User Group (RUG) to establish whether determination of corrected inherent viscosity (CIV) could be used as a standardised method in different laboratories to study PA-11 ageing. The aim of this work was to demonstrate that viscosity measurements could be reproduced in different laboratories, each with different degree of experiences with such measurements.

The work was organised as a Round Robin exercise, with nine different participating laboratories. The measurements were intended to be done in accordance with a “Recommended Practice For Viscosity Measurement of Aged and Fresh Polyamide 11 (PA-11, RilsanTM) in *m*-cresol.” The final version of the recommended practice now given in Appendix D is based, among other things, on the input from the Round Robin.

E.2 Samples Provided for the Round Robin

Three different samples of PA-11 were provided for all laboratories. These consisted of: pellets; a new extruded pipe; and an aged pipe. On the aged pipe, laboratories were asked to analyse samples from the outer and inner surfaces, and from the middle part of the sheath.

E.3 Results of the Round Robin

A summary of the determined average CIV-values are given in Table E.1, based on measurements from nine different laboratories.

Table E-1—Round Robin Test Results

Sample	Mean [dl/g]	Standard deviation	Median [dl/g]
Pellets	1.48	0.04	1.48
Extruded pipe	1.98	0.07	2.00
Aged pipe (inner)	1.20	0.05	1.18
Aged pipe (middle)	1.26	0.03	1.26
Aged pipe (outer)	1.45	0.07	1.45

E.4 Conclusions

Results show that CIV can be reproduced quite well in different laboratories. For all test samples, the maximum deviation from the mean value is 8%. The small variations between the different laboratories strongly points to the robustness of this method, and the ability to use measurements of CIV as a standard method to follow RilsanTM ageing.

It should be noted that three laboratories also measured molecular weights of the PA-11 samples using Size Exclusion Chromatography coupled to a Multi Angle Laser Light Scattering detector (SEC-MALLS). For the highest molecular weights, variations of approximately 20% were seen in the measured weight average molecular weights, whereas for the lowest molecular weights, the variation was around 10%. This rather large variation compared to the measured CIV-values, combined with the fact that expensive equipment and experienced personnel are needed to run the SEC-MALLS, further confirm the use of viscosity measurements as a standardised method to follow PA-11 ageing.

APPENDIX F—VALIDATION OF INITIAL ACCEPTANCE CRITERION THROUGH DOCUMENTED FIELD EXPERIENCE

F.1 General

The Appendix summarises available data concerning the investigation of PA-11 pressure sheaths of lines retrieved from field applications, and draws conclusions regarding an appropriate initial acceptance criterion. It is important to note that all failures of PA-11 pressure sheaths described in this Appendix have led to limited leakage of the pipe, and never to catastrophic failure.

F.2 Investigation 1

Three static lines were analysed, with only one showed brittle cracks on marks 0 and 400 m.

The service temperature was estimated at 105°C. The duration in service was 2 years. The fluid was crude oil and water. The corrected inherent viscosity (CIV) of the inner surface of the pressure sheath was 0.81 dl/g.

F.3 Investigation 2

A riser leaked due to a failure of the pressure sheath under the end fitting. The fracture was all around the circumference of the sheath. CIV measurements ranged from 1.05 dl/g to 1.11 dl/g. The viscosity gradient in end fitting was low as a result of the low temperature gradient caused by the presence of a bend stiffener.

Three other cracks occurred during retrieval, within the 30 meters of pipe closest to the end fitting. One crack was in the section of pipe open to air, the other two in the pipe which had been submerged in water. CIV ranged from 1.04 dl/g on the inside surface to 1.28 dl/g on the outside (using sample thickness of 0.2mm). The temperature in inner skin was estimated at 82°C and in outer skin at 68°C. The pipe was in service for 9 years.

F.4 Investigation 3

A static pipe sheath fractured over a length of 2.20 meters. Some brittle cracks occurred in the low part of the line, as well as star shape cracks during retrieval. The inner temperature was 89°C. The outer temperature of the pressure sheath was estimated at 79°C. The exposure duration at 89°C was 29000 hours i.e., 3.3 years.

The fluid was diphasic: liquid phase with water (pH = 5.2) in the low part of the pipe, gas in the high part of the line. The pipe fractured initially in the low part exposed to liquid.

The corrected viscosity near the initial failure was 0.89-1.13 dl/g, near the propagation cracks was 1.10-1.29 dl/g, and near the star shape cracks was 1.20 dl/g. The thickness to measure the inner viscosity was 0.45 mm for the initial failure and 0.5 mm for the propagation crack.

F.5 Investigation 4

A retrieved static flowline did not fail and had CIV ranging from 1.30 dl/g to 1.80 dl/g (using sample thickness of 0.24 mm). The temperature in inner skin was 83°C supposed to be constant, in the middle of the sheath 74°C and in outer skin 64°C. The pH of water was 5.3. The total duration in service was 4 years but the total duration at 83°C was unknown.

F.6 Investigation 5

A jumper was retrieved after 9.5 years in service. No failure has been found although the sheath had reached a critical ageing level. CIV ranged from 1.10 dl/g to 1.82 dl/g (using sample thickness of 0.22 mm). The pH was 5.3. The temperature was in average around 80°C with peaks at 110°C. The total service with “wet” flow was 7 years i.e., 73.7% of the total life. The pipe was operational for 6.8 years of this 7, i.e., 72% of the service life.

F.7 Investigation 6

A riser showed a leak of the pressure sheath under the stiffener, with CIV ranging from 0.94 dl/g to 1.54 dl/g (using sample thickness of 0.66 mm). Some propagation failures occurred as well as star shape cracks. The fluid was export oil with water. The service temperature was 83°C but measurements indicate that the flexible supported a temperature higher than 100°C (most probably 105°C). The TAN (acidity index) was 1.5 mg KOH/g.

F.8 Investigation 7

A gas injection riser, permanently exposed to injected methanol (10 litres/hour) at 60°C for 5 years has been retrieved and investigated due to concerns with respect to methanol ageing. The temperature gradient across the inner sheath was approximately 10°C. The methanol vapour was most probably not saturated.

There was no failure. The inner sheath was in good condition (e.g., elongation at break app. 300%). CIV of inside surface was 1.48 dl/g, while the outside surface was 1.62 dl/g.

F.9 Investigation 8

A flexible production riser was in service for 2.5 years. During operation the operating temperature increased from 66°C to more than 85°C. At the same time water cut increased from less than 0.1% to more than 80%. The total duration with water was more than 2 years. CO₂ partial pressure was 0.8 bar, with an average estimated total pressure at 45 bar.

There was no failure. The inner sheath material has been examined and elongation at break was app. 250 %. CIV of inside surface was 1.18 dl/g, while the outside surface was 1.42 dl/g.

F.10 Investigation 9

A flexible production riser was in service for 2.5 years. During operation the operating temperature increased from 65°C to more than 95°C. At the same time water cut increased from less than 0.1% to more than 70%. The total duration with water was more than 2 years. CO₂ partial pressure was 0.8 bar, with an average estimated total pressure at 45 bar.

There was no failure. The inner sheath material has been examined and elongation at break was 62 %. CIV of the inside surface was 1.20 dl/g, while the outside surface was 1.45 dl/g (as measured by the Round Robin exercise reported in Appendix E).

F.11 Investigation 10

Two 3-in. ID flexible flowlines were retrieved after six years service as subsea flowlines to transport production fluid from the same wellhead. The pipes did not fail during service or retrieval. The fluid temperature was estimated to be 83°C.

Two liner samples were taken from each flowline, one from the end-fitting area and one from several meters from the end-fitting. The liner ID CIV values are 1.38 and 1.25 in the end-fitting area and 1.34 and 1.33 outside the end-fitting area.

F.12 Investigation 11

A gas injection flexible riser was retrieved after 3 years in service. It was initially used 7 days for oil production with water saturated oil, pH 6 at 97°C. After 7 days, CIV was determined to be 1.87dl/g. After that the flexible riser was used for gas injection until it was taken out of operation after 3 years. Temperature profile is available for a period of 1 year, the temperature varying in the range 73 to 79°C. Methanol was used in both batch and continuous injection. Monoethylene Glycol was injected during the last year in operation.

There was no failure. CIV values in the range 1.24 – 1.77 dl/g were determined. The upper part of the riser, exposed to the highest temperature, was most degraded.

F.13 Conclusions

Review of industry experience shows that when the most highly degraded surface of a PA-11 pressure sheath goes below CIV = 1.00 to 1.05 dl/g it is likely to fail (see below).

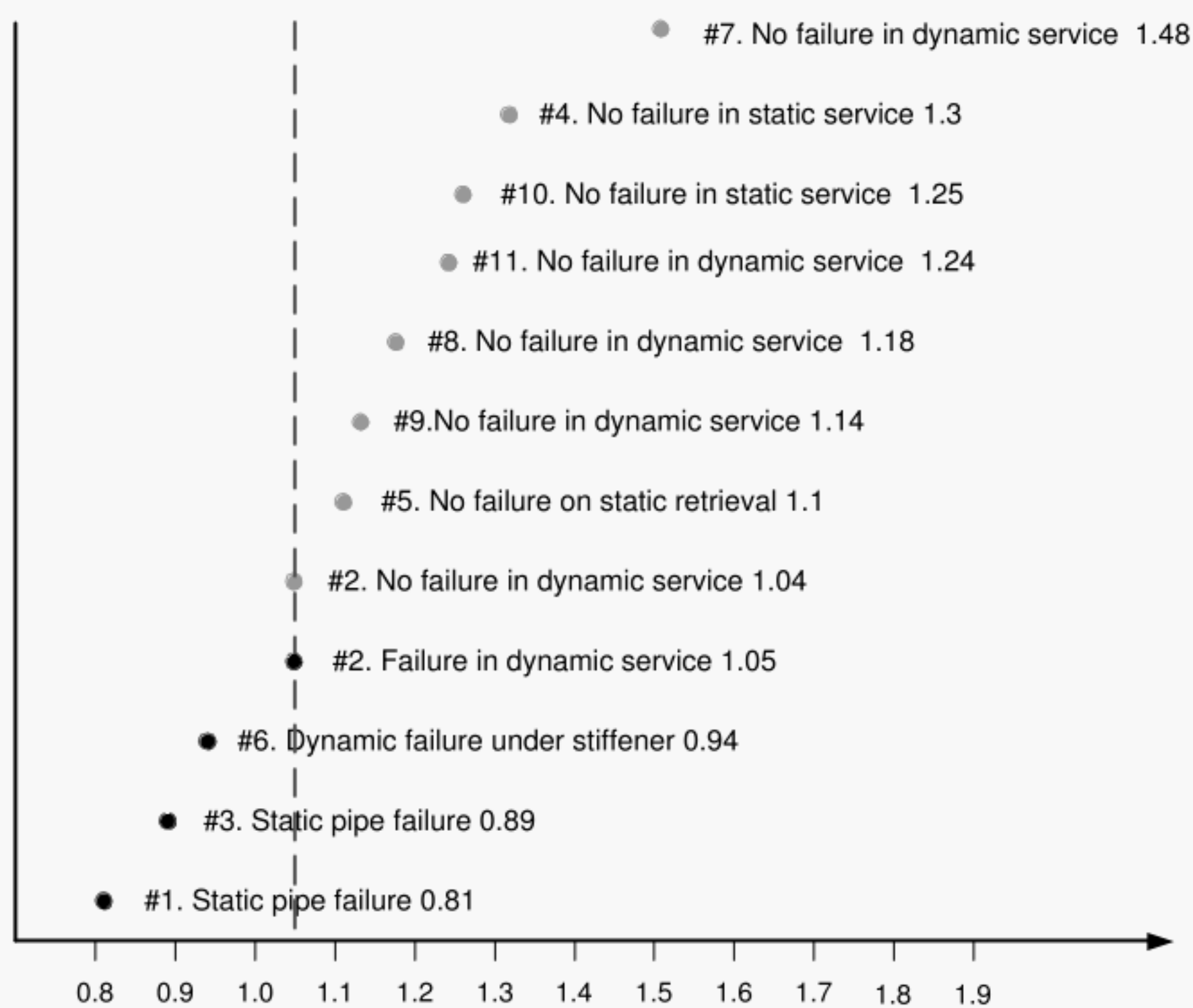


Figure F-1—Correct Inherent Viscosity dl/g

APPENDIX G—VALIDATION OF INITIAL ACCEPTANCE CRITERION THROUGH LABORATORY CONSIDERATION OF FATIGUE AND FRACTURE MECHANICS

G.1 General

Pressure sheath failures have tended to initiate with a crack parallel to the interior extrusion ribs, which grows into either a brittle crack with bifurcations (“star crack”) or a fatigue crack with banding. In addition, several failures have initiated at defects in the end-fitting caused by machining during end fitting assembly. It is important to note that the topside end-fittings, under bend stiffener and/or fire insulation, can be a hot spot of the pipe, such that thermal degradation due to hydrolysis may be particularly severe.

In order for a crack to occur in the pressure sheath, a stress must be imposed on the “defect.”

G.2 Sources of Stress

There are several possible sources of stress in the pressure sheath:

- Thermal stress**—Thermal stress in PA-11 is very small. The expansion coefficient is $11 \times 10^{-5} \text{ K}^{-1}$ between -20 and 50°C and $23 \times 10^{-5} \text{ K}^{-1}$ between 50 and 130°C .
- Bending stress**—This is the source of greatest stress on a pressure sheath. Strain during spooling is limited to 7.7% by API Spec 17J. The geometry of the extrusion ribs on the inner surface can lead to significantly higher localised triaxial deformation at the base of the ribs, which is thought to have been responsible for many observed failures.
- Hoop stress due to a change in pressure within the pipe**—Ideally, hoop stress should be taken by the armour wires. Some hoop stress may be exerted on the pressure sheath due to rapid pressure changes and the small degree of freedom of the sheath between the carcass and the armour wires.
- Pressure sheath creep**—The pressure sheath is subject to creep into gaps between wires, setting up stress fields.
- Clamping stress within the end-fitting**—The stress exerted in the end-fittings is mainly due to compression. In some designs a certain degree of local movement is allowed. Otherwise, the main concern is creep.

G.3 Sources of Defects

Defects in the pressure sheath can have 3 origins:

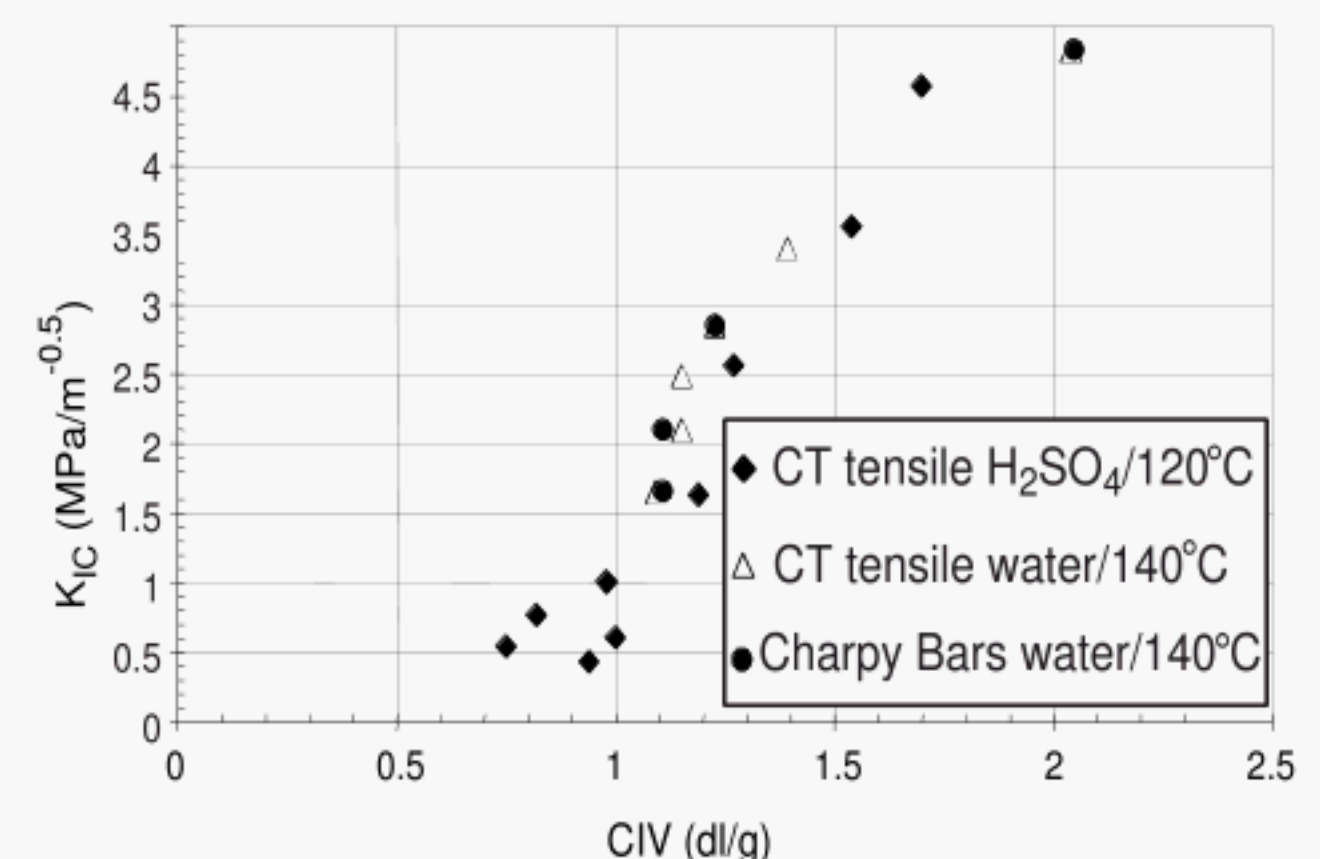
- External cut, dent or roughness due to machining or handling**—External defects can be monitored. Machining can be controlled to specific surface roughnesses.
- Embedded inclusion**—Failures due to inclusions are not known. Extruded PA-11 pipes can be easily inspected for inclusions due to the translucency of the material.
- Interior extrusion ribs.**

The fact that most initial cracks originate in the line parallel to the extrusion ribs without any apparent “defect” demonstrates that defects are mostly well controlled and that the material is tolerant of the extruded surface geometry.

G.4 Fracture Toughness

In its as-new condition, PA-11 generally fractures in a ductile fashion. Brittle failure has only been observed on material which has been considerably aged. Test data demonstrates a correlation between K_{IC} and molecular weight as measured by inherent viscosity (see Table G.1).

Table G-1—Comparison of K_{IC} Values Obtained on Compact Test Specimen and Charpy Bars Aged in H_2SO_4 pH 4 at 120°C and Water at 140°C

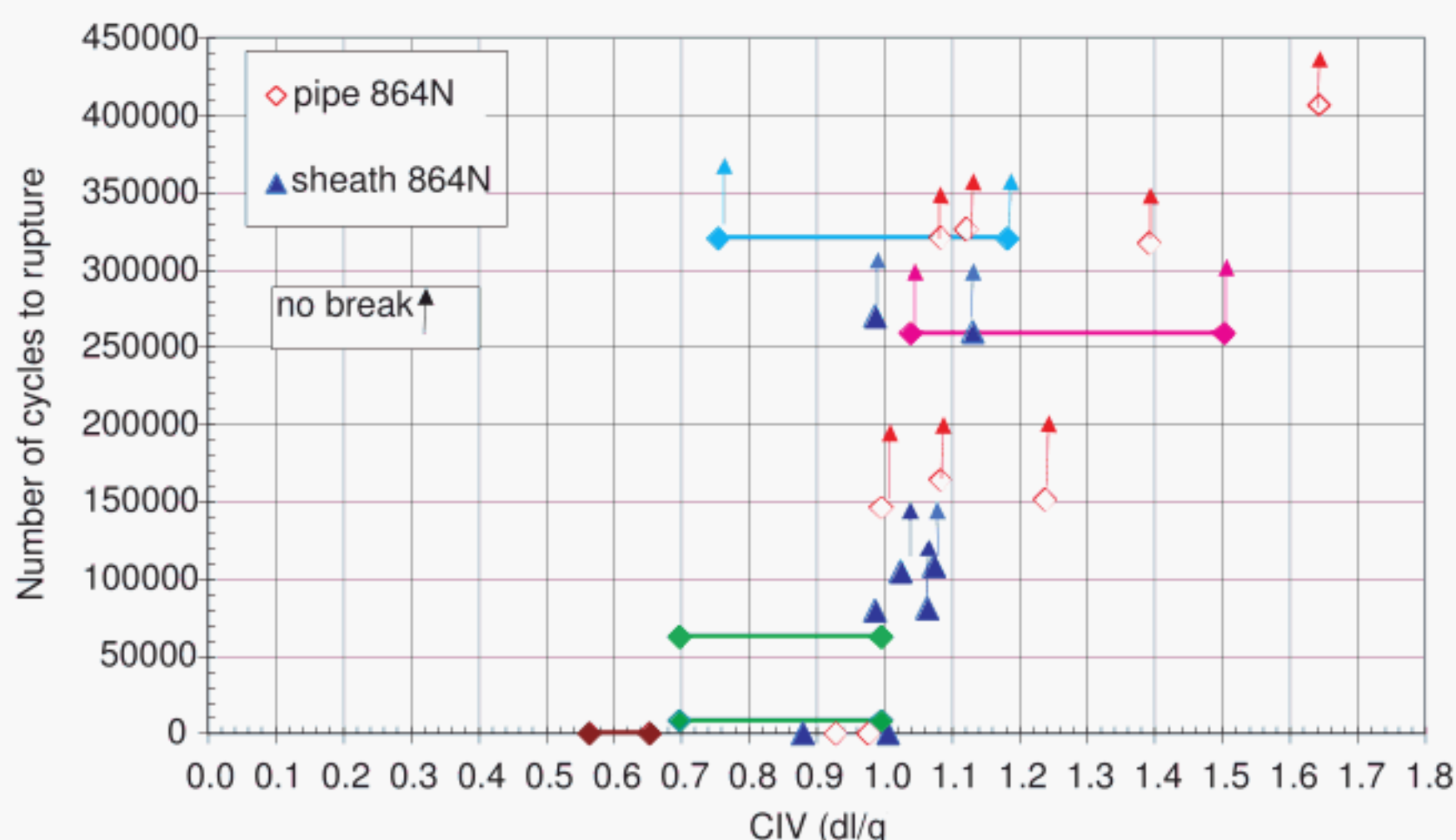


Analysis of fracture faces has shown three types of behaviour:

Fully Ductile	$K_{IC} \geq 3$	$CIV \geq 1.2$	PA-11 tough and very tolerant to defects. No failure have been observed in this region.
Ductile / Brittle	$1 \leq K_{IC} \leq 3$	$1.0 \leq CIV \leq 1.2$	
Fully Brittle	$K_{IC} < 1$	$CIV < 1.0$	PA-11 is very brittle.

In the brittle condition, K_{IC} drops to around 0.5. For stress levels which might easily be seen as a result of bending, e.g., 5 MPa, critical notch size is ~ 4 mm. In the case of a higher stress such as 10 MPa a critical notch size of as low as 0.08 mm will lead to a brittle failure.

Table G-2—Tensile fatigue: Samples Cut from Pipe and Sheath Aged in Benzoic Acid at 120°C



G.5 Fatigue

Fatigue experiments have been performed on aged sections of pressure sheath, including internal “ribs” and smooth bore pipes (see Table G.2). (Starting strain = 4 % corresponding to 12.5 MPa. Stress controlled fatigue cycles 1 Hz (maximum frequency without self heating) between 10 and 100 % of imposed maximum stress.

The bars indicate viscosity gradients over the sheath thickness. A rapid drop in fatigue resistance is observed at a CIV = 1.0. Below this value the material is essentially brittle.

It can be observed that no significant differences exist between the fatigue resistance of smooth samples (open symbols) and samples with an extrusion rib (closed symbols). This demonstrates the high defect tolerance of PA-11 which is not totally aged.

G.6 Conclusion of Fracture Toughness and Fatigue Testing

Above CIV = 1.2, PA-11 is fully ductile and fit for use in flexible pipe, while below CIV = 1.0 it is brittle and may be unfit for service.

In the region $1.0 \leq \text{CIV} \leq 1.2$, a ductile / brittle transition as a function of temperature and strain rate is currently under construction, to guide operations with highly aged pipes.

This is a conservative approach. A more detailed fracture mechanics approach, taking account of real stress and strain in the pipe could be developed with time. This is not a simple undertaking on account of highly non-linear and time dependent mechanical behaviour of PA-11, and the difficulty in calculating actual stress and strain.

G.7 Literature on Fracture Mechanics

1. ISO task group working on the compact test K_{IC} method: ISO/TC61/SC2 n° 572.
2. J.G. Williams testing *Protocol*, March 1990, Mech. Eng. Dept. Imperial College, London.
3. ASTM E 399-81 *Standard Test Method for Plane Strain Fracture Toughness of Metallic Materials*.
4. J.G. Williams, M.J. Cawood, *Polym. Testing*, 9, 15 (1990).
5. J.G. Williams, “Fracture Mechanics of Polymers,” Ellis Horwood Ltd., Chichester (1984).

APPENDIX H—RISER WORKED EXAMPLE

A 500 m.-long, 6" flexible production riser, handles 5000 bpd of three-phase production.

The flexible pipe structure has an insulation factor of 9 W/m/K, as a result of which the fluid temperature decreases slightly along the pipe.

The production temperature profile is estimated to be:

Years 1 to 6: 58°C (at the riser base) with a pH value of 5

Years 7 to 10: 65°C (at the riser base) with a pH value of 6

To determine the contribution of each of these periods to the ageing of the PA-11 sheath, Miner's Rule is used.

Under the conditions for the first 6 years, the time for the PA-11 sheath to reach the initial acceptance criterion of CIV=1.2dl/g according to the curves in section 3.4 is 30 years. Thus, in the first 6 years of service, the proportion of this time which is expended is $(6 / 30) = 0.20$.

For years 7 to 10, the time for the PA-11 sheath to reach the initial acceptance criterion of CIV=1.2dl/g is 17 years. This in these 4 years, the proportion of this time expended is $(4 / 17) = 0.24$.

To assess the cumulative ageing, the two periods are summed, giving $S = 0.2 + 0.24 = 0.44$.

The PA-11 sheath is close to half way to the initial acceptance criterion. If $S \geq 1$, the initial acceptance criterion is reached.

In addition, we can calculate the remaining time needed to reach the initial acceptance criterion for a given combination of temperature and pH.

$$\begin{aligned} \text{(Remaining time to reach CIV = 1.2 dl/g)} \\ = (1-S) * (\text{Time to reach CIV = 1.2 dl/g at} \\ \text{service T and pH}). \end{aligned}$$

Thus, for example, if after year 10, the temperature is 70°C and pH is 6,

$$\begin{aligned} \text{(Remaining time to reach CIV = 1.2 dl/g)} \\ = (1 - 0.44) * 9 \text{ years} = 5.1 \text{ years.} \end{aligned}$$

By this method, the contribution of many different periods can be assessed, e.g., production periods with different durations temperatures and pH, and also methanol batch periods, and the remaining time for the PA-11 pressure sheath to reach CIV = 1.2 dl/g calculated.

If in this case coupons are installed topsides, the insulation effect of the riser needs to be taken into account.

In case of coupons installed at the platform (coldest extremity) to follow the RilsanTM ageing. In this example, the temperature is 50°C at the platform for the first 6 years, and 56°C for the subsequent four, calculated taking into account the insulation factor of the pipe, its length and structure, the fluid composition and the flowrate. Comparison of calculated and measured corrected inherent viscosity of the coupons is typically in good agreement.

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